Conformation of Aminals Derived from Arylamines and Methanal

by

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Summary

In this thesis, the poly-condensation, which takes place between formaldehyde and arylamine under basic conditions, is studied by establishing the structures of the 2:1 adducts (34) and (36) and the cyclic 3:3 adducts (32), (41), (43) and (45) by X-ray crystal structure analysis and spectroscopic methods.

The presence of electron-withdrawing substituents ortho or para to the amino group of the arylamine promotes, in some cases, termination of the poly-condensation at the 2:1 adduct stage but the potential stereochemical blocking effect of an electron-donating substituent on the arylamine ortho position does not hinder the formation of higher adducts. The further poly-condensation observed of certain 2:1 adducts bearing electron- withdrawing substituents are interpreted as the result of variations in the nitrogen atom basicity, polarity and solubility. Reaction of those arylamines, which above gave 2:1 adducts, with dimethyl sulphoxide/ phosphorus pentoxide did not yield cyclic 3:3 adducts.

The 2:1 adducts isolated show that in the solid state N,N bis-(2-trifluoromethylphenyl)-diaminomethane (36) adopts a skewed conformation around both N–CH_2 bonds.The N–CH_2 bond is rotated out of the plane of the adjacent phenyl ring to a small extent. The bond angles in the chain linking the phenyl groups are distinctly greater than tetrahedral.The N–CH_2 are longer than the N–C(aryl) bonds, similar values for N–C(aryl) bonds have been observed in N,N–dialkylanilines with electron-withdrawing substituents on the phenyl rings. In the trifluoromethyl groups the F–C–F angles are all smaller than tetrahedral. The short H...F distance between the H atoms on N(A) and N(B) and the F atoms of the adjacent CF_3 may represent intramolecular hydrogen bonding since there is no intermolecular hydrogen bonding.

The cyclic 3:3 adducts isolated all adopt the twin-chair conformation with the substituents in the *aae* conformation. The N–C(axial) bonds in the o-OMe and p-OMe compounds are bent outwards by 15-24° from the ideal chair conformer , reducing the interactions

between the axial aryl groups.The orientations of the aryl groups about the N–C(aryl) bonds reflect the increased steric requirements when the aryl group is changed from p- to o-methoxyphenyl. The packing of the o-substituted molecules in the unit cell is rather more compact than that of the p-substituted molecules.

The cyclic 3:3 adduct from 4-nitroaniline , formed by the reaction of the latter with dimethyl sulphoxide/pentoxide, crystallised from pyridine as a 1:1 inclusion compound in which the 1,3,5-triazacyclohexane ring exists in a twist-boat conformation and the unit cell contained four molecules of 1,3,5,tri(p-nitrophenyl)-1,3,5 triazacyclohexane and four molecules of pyridine. The pyridine molecules occupy open-ended spiral channels. The N-C(aryl) bonds from the triazacyclohexane nucleus in the p-nitrophenyl compound are tilted at 21.2, 29.5 and 3.3(3)° to the CH_2-N-CH_2 planes at N(1), N(3) and N(5), respectively, so that the arrangement of N-C bonds is coplanar at only one of the N atoms, N(5). These out-of-plane angles are, nevertheless, smaller than the angles in other triazacyclohexanes. Though the conformation departs a little from the ideal twist-boat form, presumably in response to crystal packing requirements a substituted twist cyclohexane shows a similar skewing. Because the unsolvated cyclic 3:3 adduct from 4-nitroaniline gave only poor crystals , its solid-state conformation was not available for comparison. Attempts to prepare other solvates of the cyclic 3:3 adduct have so far been unsuccessful. Based on the above evidence for the formation of 2:1 and 3:3 arylamine- formaldehyde poly-condensed structures, together with other work in this laboratory on cyclic 3:3 adducts and the reported isolation of 1:1, cyclic 2:2 and cyclic 4:4 products, a speculative mechanism is proposed for the stepwise poly-condensation of formaldehyde and arylamine involving nucleophilic additions to aldehyde, imine and imnium double bonds.

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Compound List

1. N-Methyleneaniline
2. Cyclic dimer (1,3-Diphenyl-1,3-diazacyclobutane)
3. Cyclic trimer (1,3,5-Triphenyl-1,3,5-triazacyclohexane)
4. N-methylene-2,6-di-isopropylaniline
5. Polyoxymethylene
6. 2,6-di-isoproplyaniline
7. Cyclic trimers , i.e 1,3,5-Triaryl-1,3,5-triazacyclohexanes
8. 1,3,5-Trimethyl-1,3,5-triazacyclohexane
9. 1,3,5-Tribenzyl-1,3,5-triazacyclohexane
10. 1,3,5-Tri-(*o*-fluorophenyl)-1,3,5-triazacyclohexane
11. 1,3,5-Tri-(*m*-fluorophenyl)-1,3,5-triazacyclohexane
12. 1,3,5-Tri-(*p*-fluorophenyl)-1,3,5-triazacyclohexane
13. 1,3,5-Tri-(*o*-chlorophenyl)-1,3,5-triazacyclohexane
14. 1,3,5-Tri-(*m*-chlorophenyl)-1,3,5-triazacyclohexane
15. 1,3,5-Tri-(*p*-chlorophenyl)-1,3,5-triazacyclohexane
16. Cyclic tetramer (1,3,5,7-tetraphenyl-1,3,5,7-tetraazacyclooctane)
17. NO_2 tetramer
18. Ph tetramer

19. EMeCO tetramer

20. 1,3,5-Tri-(4-nitrophenyl)-1,3,5-triazacyclohexane

21. N,N-bis-(4-nitrophenyl)-diaminomethane

22. 1,3,5-Tri-(4-nitrophenyl)-1,3,5-triazacyclohexane:pyridine (1:1) inclusion compound

23. Cyclohexane-1,4-dione

24. N,N-dimethylaniline

25. *p*-nitro-N,N-dimethylaniline

26. 1,3,5-Triacetyl-1,3,5-triazacyclohexane

27. Humulene nitrosite

28. 3,3,6,6-Tetramethyl-1,2,4,5-tetrathiane

29. Hexakis (p-t-butylphenylthiomethyl) benzene

30. 1,3-Dihydroxymethyl-5-t-butylcyclohexane

31. 1,3,5-Tri-(4-acetylphenyl)-1,3,5-triazacyclohexane

32. N,N-bis(4-acetylphenyl) diaminomethane

33. 1,3,5-Tri-(4-methoxycarbonylphenyl)-1,3,5-triazacyclohexane

34. N,N,-bis(4-methoxycarbonylphenyl)-diaminomethane

35. 1,3,5-Tri-(2-trifluoromethylphenyl)-1,3,5-triazacyclohexane

36. N,N bis-(2-trifluoromethylphenyl)-diaminomethane

37. 4-Dimethylaminoazobenzene-2-carboxylic acid

38. 4-Dimethylamino-3-nitrocinnamic acid

39. N,N-di-n-propyl-2,6-dinitro 4 chloroaniline

40. 1,3,5-Tri-(3-trifluoromethylphenyl)-1,3,5-triazacyclohexane

41. 1,3,5-Tri-(4-cyanophenyl)-1,3,5-triazacyclohexane

42. 1,3,5-Tri-(4-benzoylphenyl)-1,3,5-triazacyclohexane

43. 1,3,5-Tri-(2-methoxyphenyl)-1,3,5-triazacyclohexane

44. 1,3,5-Tri-(3-methoxyphenyl)-1,3,5-triazacyclohexane

45. 1,3,5-Tri-(4-methoxyphenyl)-1,3,5-triazacyclohexane

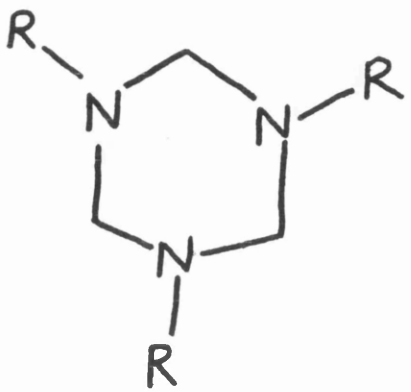
46. 1,3,5-Triphenyl-1,3,5-triazacyclohexane

47. 1,3,5-Tricyclohexyl-1,3,5-triazacyclohexane

48. *p*-Fluoroaniline

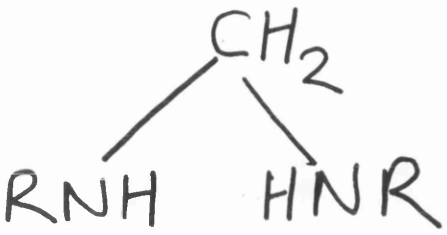
FORMULAE

Triazacyclohexanes



3	R = C_6H_5	8	R = CH_3
10	R = *o*-C_6H_4F	11	R = *m*-C_6H_4F
12	R = *p*-C_6H_4F	13	R = *o*-C_6H_4Cl
15	R = *p*-C_6H_4Cl	20	R = *p*-$C_6H_4NO_2$
26	R = OCH_3	31	R = *p*-$C_6H_4COCH_3$
33	R = *p*-$C_6H_4COOCH_3$	35	R = *o*-$C_6H_4CF_3$
40	R = *m*-$C_6H_4CF_3$	41	R = *p*-C_6H_4CN
42	R = *p*-C_6H_4COPh	43	R = *o*-$C_6H_4OCH_3$
44	R = *m*-$C_6H_4OCH_3$	45	R = *p*-$C_6H_4OCH_3$

Diaminomethanes



21 R = *p*-$C_6H_4NO_2$

32 R = *p*-$C_6H_4COCH_3$

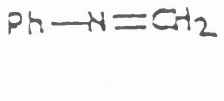
34 R = *p*-$C_6H_4COOCH_3$

36 R = *o*-$C_6H_4CF_3$

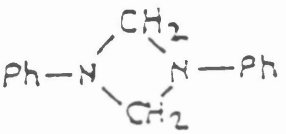
Chapter 1

Introduction

N-Methyleneaniline (1) is an elusive compound. Although a patent claimed its preparation in the pure crystalline state the misidentification is now all too obvious: the substrate obtained was the now well established cyclic trimer (3), which can be obtained under a variety of experimental conditions from aqueous formaldehyde or paraformaldehyde and aniline and there is also the possibiltiy of a cyclic dimer (2) being formed form this reaction. There is some indication that both (1) and (2) might exist in equilibrium with (3). N-Methyleneaniline (1) usefulness may be limited because of its instability, but could be a reactive synthon if formed *in situ* by e.g. the pyrolylic degradation of (3).



1



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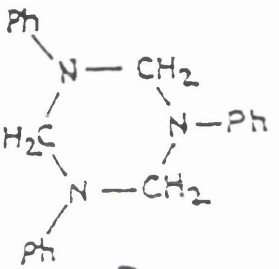
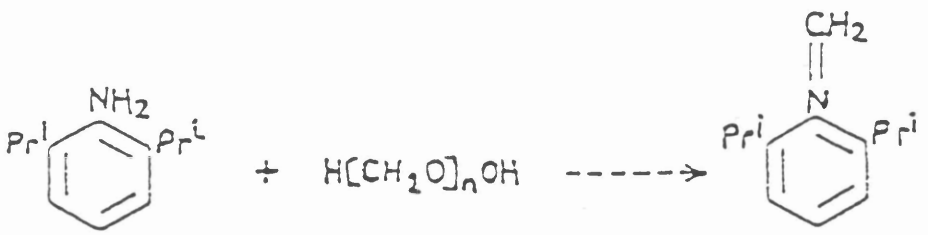


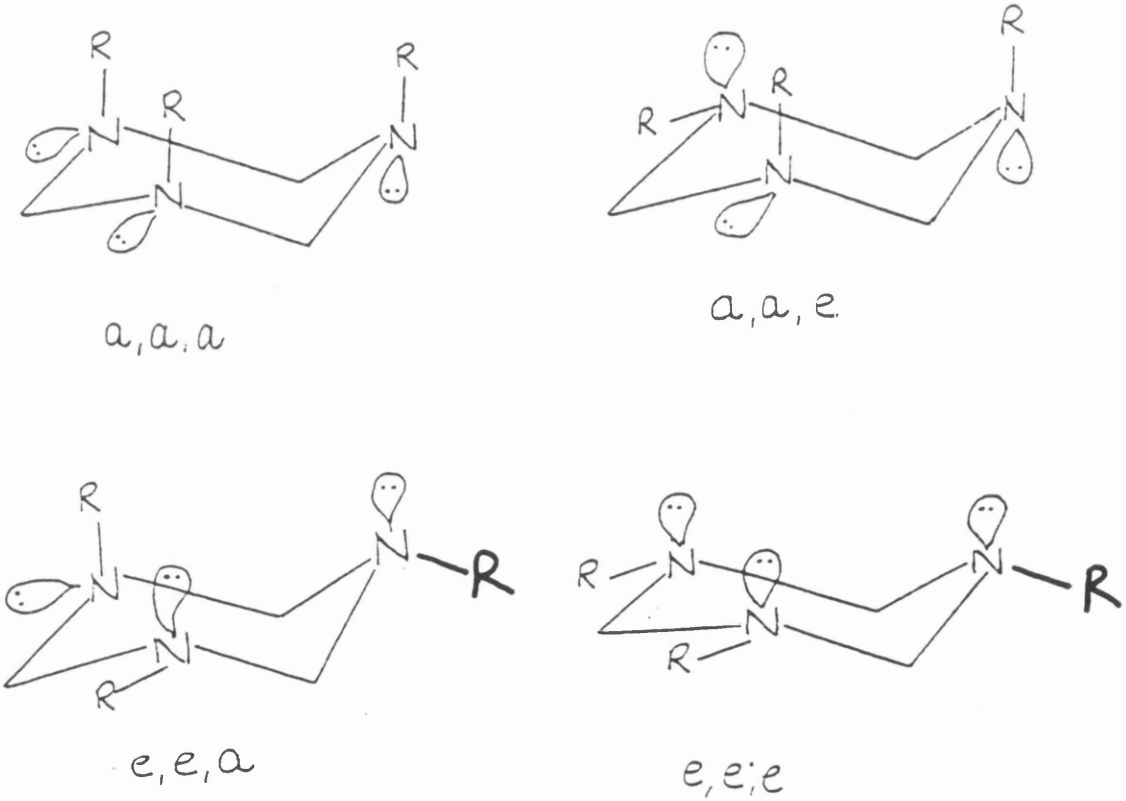
3

The first free monomeric N-methylene aromatic amine stable under normal conditions in the solid or liquid state and authenicated by analytical and spectroscopic data is N-methylene-2,6-di-isopropylaniline (4) (Verardo , Cauci & Giumanini , 1985). This was prepared by heating equimolar amounts of polyoxymethylene (5) and 2,6-di-isopropylaniline (6).



6 5 4

The cyclic trimers (7) , i.e 1,3,5-Triaryl-1,3,5-triazacyclohexanes were first prepared more than a century ago (Wellington & Tollens 1885) but their conformations have only recently been investigated. X-ray investigations of 1,3,5-triaryl derivatives of 1,3,5-triazacyclohexane have consistently found the expected chair conformation with pyramidal arrangement of bonds at N atoms (Giumanini,Verardo, Randaccio, Bresciani-Pahor & Traldi, 1985; Zangrando, Poggi, Giumanini & Verardo, 1987; Giumanini, Verardo, Zangrando & Lassiani, 1987;Sim 1987; Bouchemma, McCabe & Sim, 1988, 1989, 1990.).
In the chair conformation four patterns of substituent orientations at the hetero atom have to be considered *aaa* , *aae* , *aee* , *eee* where *a* = axial and *e* = equatorial (see Fig 1,2,3 and 4). Each of these conformations has 1-3-di axial interactions involving the lone pair of electrons and/or the substituents on the N atoms and the *aae* appears to be preferred.



Figs 1,2,3 and 4

The conformation of 1,3,5-trialkyl-1,3,5-triazacyclohexanes in solution have been investigated by dipole moment and NMR spectroscopy methods, the former approach suggesting varying amounts of *aae* , *aee* , *eee* conformers (Jones, Katritzky & Snarey 1970 ; Duke, Jones, Katritzky, Scatterwood & Riddell 1973) but subsequent ^{1}H and ^{13}C NMR studies of the trimethyl compound (8) at various temperatures were interpreted in terms of a predominant *aee* conformer (Bushweller, Lourandos & Brunelle 1974 ; Baker, Ferguson, Katritzky, Patel & Rahimi-Rastgoo 1978).

The tribenzyl compound (9) has been studied by X-ray crystallography at several temperatures (Sim 1987). On lowering the temperature of the crystal the cell dimensions and cell volume changed smoothly with no indication of phase change; the β angle of the monoclinic cell, for example, increased from 109.0° at 293K to 116.5° at 127K . The crystal structure at 127K, the lowest temperature investigated proved to be ordered with a single conformer *aae* present. At 250K only traces of other conformations were present, whereas at 268K the disorder was pronounced with significant populations of the axial and equatorial sites at each nitrogen atom (Table 1). The changes in the occupation of the axial and equatorial sites as the temperature is altered establish that the nitrogen inversion is occurring in the solid at room temperature and immediately below. It is not possible to specify the precise mixture of molecular conformers (*aaa* , *aae* , *eea* , *eee*) present at higher temperatures, but if it is assumed that *eee* and *aaa* can be disregarded because of repulsion between axial substituents in the latter and lone pairs of electrons in the former, the temperature- dependent molecular process is $eaa \rightleftharpoons eea$ then the conformational composition can be seen in (Table 1) below.

Table 1

The changes in the occupation of the axial and equatorial sites of tribenzyl compound (9) as the temperature is varied.

TEMPERATURE	% eaa	% eea
293 K	54	46
268 K	74	26
250 K	92	8
127 K	100	0

In order to study the conformational response to varying steric requirements in 1,3,5-triaryl-1,3,5-triazacyclohexanes the *o*, *m*, and *p*–fluorophenyl (10,11,12) and the *o*- and *p*-chlorophenyl compounds (13,15) were prepared and their molecular geometries examined by X-ray diffraction (Bouchemma, McCabe & Sim).

In the solid state, the *p*-fluoro compound (12) exists in the *aae* conformation and has the equatorial aromatic ring in the ideal perpendicular orientation, the angle between the aromatic ring and the symmetry plane of the triazacyclohexane ring being 90°. In the *m*-fluoro compound (11) (*aae* conformation), the appropriate angle is 54.7° and, in the *o*-fluoro compound (12) (*aae* conformation), it is 22.5°. The change in orientation of the substituted phenyl ring clearly mirrors the increasing steric requirements as the aryl group is changed from *p*- to *m*- to *o*-fluorophenyl. The effect on the axial aryl groups is less pronounced though there is an indication of steric effects since the orientation changes from 61–65° in the *p*- and *m*-fluorophenyl compounds to 44–46° in the *o*-fluorophenyl compound.

The N atoms are distinctly pyramidal in character and the N–C(aryl) bonds are inclined to the appropriate CH_2–N–CH_2 planes at 32.6–48.5° (Table 2). The largest out-of-plane angle 48.5°, is for the equatorial *o*-fluorophenyl group which is close to the parallel orientation , *i.e.* with the smallest lone-pair-π-orbital overlap.

In the triazacyclohexane ring of (10),(11) and (12) the torsion angles around the C–N bonds are in the range 52.7–59.5, mean 56.5°. The CH_2–N–CH_2 bond lengths are 1.443–1.479 , mean 1.460Å similar to those in the tribenzyl compound (9) which are 1.445–1.480, mean 1.463Å. The CH_2–N–CH_2 angles are 108.2–110.7, mean 109.7° and the N–CH_2–N angles are 110.5– 113.0, mean 111.9°.

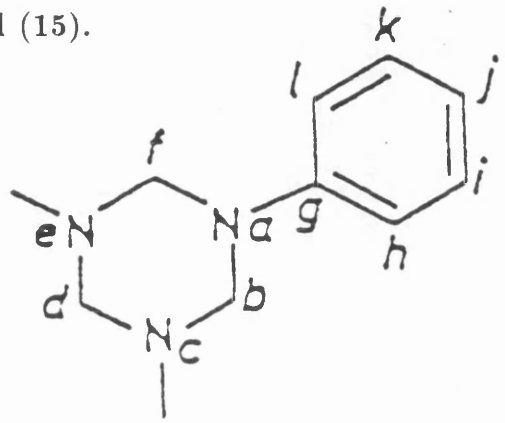
In the related group of tri(chlorophenyl)-1,3,5 triazacyclohexanes (13),(14) and (15) the *m*-compound (14) has not been reported , and the *o*-chloro (13)and the *p*-chloro (15) both exist in the *aae* conformation in the solid state. In the *p*-chlorophenyl compound (15) the angle between the equatorial aromatic ring and the symmetry plane of the triazacy-

clohexane is 90° and in this conformation there is maximium overlap between the N(3) lone pair and the π orbitals of the aromatic ring. In the *o*-chlorophenyl compound, in contrast, the equatorial aromatic ring lies in the symmetry plane of the molecule so that there is no overlap between the N(3) lone pair and the π orbitals of the aromatic ring. The change in orientation can be attributted to the severe overcrowding that would arise for the Cl atom if the *o*-chlorophenyl compound (13) adopted the orientation of the *p*-chlorophenyl compound. The substituent position also affects the axial aryl groups since the orientation angle θ changes from 68.1° in the *p*-chlorophenyl compound to 44.2° in the *o*-chlorophenyl compound in accord with the *o*- and *p*-fluorophenyl compounds.

The N atoms are distinctly pyramidal in character, the N–C(aryl) bonds being inclined to the CH_2–N–CH_2 planes at 32.3–48.9 °. The out-of -plane angle in a tetrahedral arrangement of bonds is 54.7° and out-of-plane angles of 32.3– 35.3° indicate the N–C(axial) bonds in the *o*- and *p*-chlorophenyl compounds are bent outwards by 19–22° from the positions in an ideal chair conformation.

Table 2

Conformational details of *o*, *m*, and *p*–fluorophenyl (10),(11) and (12) and the *o* and *p*-chlorophenyl compounds (13) and (15).



θ is the angle between planes **dagj** and **aghijkl**

γ is the angle between bond **a–g** and plane **fab**

ζ is the angle between bond **a–g** and plane **ghijkl**

		θ (°)	γ (°)	ζ (°)
o-Fluoro	N(5) equatorial	22.5	48.5	0.9
(10)	N(1) axial	45.7	35.9	5.4
	N(3) axial	44.1	33.7	5.6
m-Fluoro	N(1) equatorial	54.7	32.6	4.8
(11)	N(3) axial	64.3	36.7	2.1
	N(5) axial	65.3	37.4	2.9
p-Fluoro	N(1) equatorial	90.0	36.9	4.6
(12)	N(3) axial	61.3	37.4	2.2
	N(5) axial	61.3	37.4	2.2
o-Chloro	N(3) equatorial	0.0	48.9	0.0
(13)	N(1) axial	44.2	35.3	4.1
p-Chloro	N(3) equatorial	90.0	35.5	6.5
(15)	N(1) axial	68.1	32.3	5.2

The cyclic tetramer (17) of an N-methyleneaniline was first isolated in 1963 (Cady Larsen & Cromer, 1963) and since then other two tetramers (18, 19) have been reported (Giumanini, Gei, Randaccio & Zangrando, 1987; Choi, Abel, Dickens & Stewart, 1973). A primary indication of the tetrameric structure of (16) was obtained from positive ion electron impact mass spectrometry at 70 eV, the spectrum exhibited a weak but distinct peak m/e 420 for the molecular ion. Similar observations were made for number of ring substituted derivatives (Table 3). The X-ray diffraction study of (18) showed that the crystals are built up of discrete tetrameric units one of which is shown (Fig 5). The molecule is centrosymmetric being arranged about a crystallographic inversion centre.

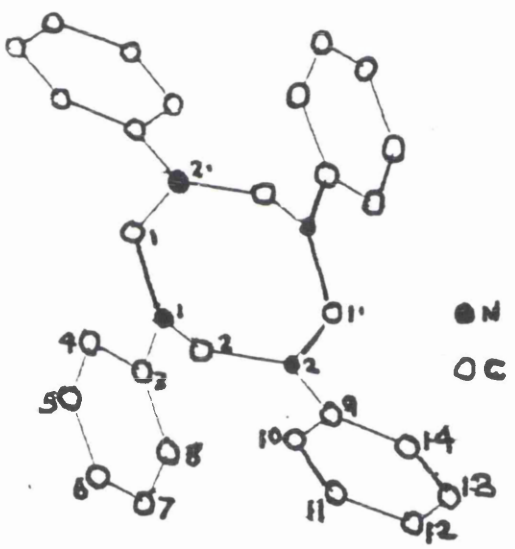


Fig 5

The N-phenyl eight membered ring has a twisted chair–like conformation (see Fig 6) with four symmetry independent torsion angles about the N*(2)–C(1), C(1)–N(1), N(1)–C(2) and C(2)–N(2) bonds of -38.5, 113.8 -108.0 and 29.7° respectively.The N-acetyl (19) eight membered ring exists as a twist crown conformation (see Fig 7).

Table 3

The conformation and geometry of tetramers (17),(18) and (19). The bond angles (°) and bond lengths (Å) are mean values.

	R	CONFORMATION	∠ N	∠ C	C–N	N–R
17a	NO_2	crown	122(2)	112(2)	1.45(1)	1.36(1)
17b	NO_2	chair	118.8(4)	111.9(4)	1.453(6)	1.364(5)
17c	NO_2	crown	115(1)	112(1)	1.47(2)	1.37(2)
17d	NO_2	crown	121.0(3)	112.7(4)	1.450(6)	1.372(5)
17e	NO_2	crown	121.8(3)	115.8(4)	1.455(4)	1.370(4)
18	Ph	chair	118.3(3)	109.5(3)	1.452(5)	1.391(5)
19	EMeCO	crown	117.5(1)	113.9(1)	1.457(2)	1.366(2)

17a α–form (Cady Larsen & Cromer, 1963).

17b β–form (Choi & Boutin, 1970).

17c δ–form (Cobbledick & Small, 1974).

17d α–adduct with DMF (Haller, Rheingold & Brill, 1983).

17e β–adduct with DMF (Cobbledick & Small, 1975).

18 (Giumanini, Gei, Randaccio & Zangrando, 1987).

19 (Choi, Abel, Dickens & Stewart, 1973).

The cyclic tetramers (Table 3) exhibit two types of conformations the twisted chair or twisted crown (Figs 6 and 7).The cyclic tetramers could also exhibit a boat-like conformation but there has been no such conformations reported.

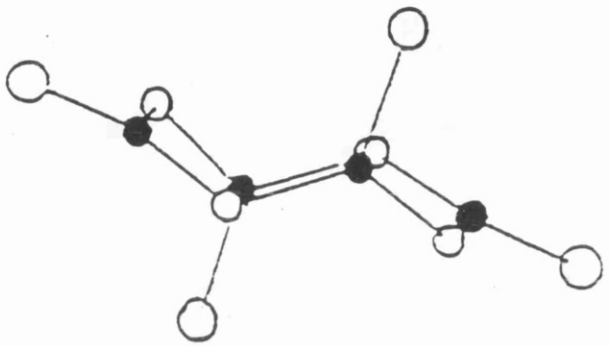


Fig 6: Twisted Chair, side view

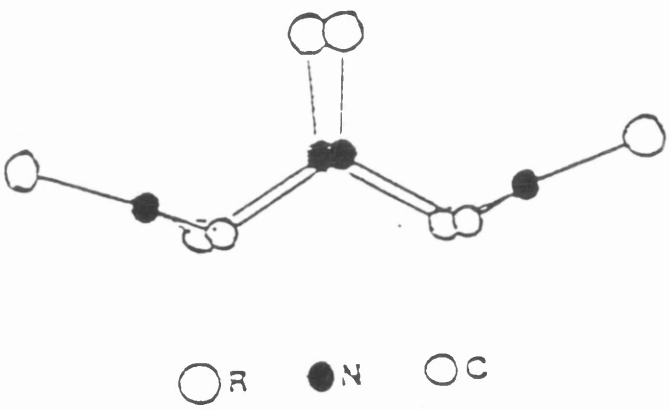


Fig 7: Twisted Crown, side view

Some structural characteristics of the eight membered ring tetramer (16) and of the trimer (3) are compared in Table 4 . The tetramer shows slightly shorter N–Ph bonds (1.391(5)Å), whereas the mean endocylic bond lengths are equal within experimental error. The difference in the N–Ph distance could be related to the significant widening of the endocyclic angles especially those at the N atoms.

Table 4

Structural characteristics of the eight membered ring tetramer (16) and of the trimer (3). The bond angles (°) and bond lengths (Å) are mean values.

	Tetramer	**Trimer**
Bond lengths		
N–C	1.452(5)	1.458(3)
N–Ph	1.391(5)	1.410 (4)
Angles		
∠ N	118.3(3)	109.5(3)
∠ C	113.6(3)	111.5(3)

Saturated heterocyclic compounds are of great interest because they offer a variety of possibilities for study of the effect of non-bonding electrons on the ring conformations by X-ray crystal structure analysis. Two such effects, the anomeric effect and rabbit-ear effect, are recoginised in structural chemistry. The anomeric effect is the greater preference of an electronegative substituent group for the axial position when it is located adjacent to a heteroatom in a ring than when it is located elsewhere. This effect has been reported in six-membered heterocyclics containing oxygen and sulphur where the electronegative group is alkoxyl or halogen (Eliel & Giza, 1968).

The rabbit-ear effect leads to a disfavouring of conformations in which unshared electron pairs on non-adjacent hetero atoms are parallel or syn-axial (Hutchins, Kopp & Eliel 1968). For example it has been shown that 1,3,5- triazacyclohexanes exist in the *aae* conformation in the solid state (Giumanini,Verado, Randaccio, Bresciani-Pahar & Traldi, 1985 : Bouchemma, McCabe & Sim, 1988.). The preference for this conformation is a consequence of the rabbit-ear effect through which the *aee* confomation is disfavoured because of 1,3 dipolar alignment of the N lone pairs.

In this project it was proposed to extend the work of Bouchemma, McCabe and Sim by examining the effect on the arylamine/formadehyde condensation reaction of placing electron withdrawing substituents e.g NO_2 on the aromatic amine component. The structures of all products are to be established as far as possible by chemical/spectrocopic analysis and where appropriate by X-ray crystal structure analysis. In the case of six-membered ring products,the X-ray analysis would provide information on the axial-equatorial preference of the nitrogen lone pairs when they are, at least potentially, delocalised.

Chapter 2

General Experimental

Formalin was of concentration 37–39 % (w/w) and absolute ethanol was 99.8 % . Benzene and toluene were both dried over sodium wire . Methanol was dried by the addition of a few grams of magnesium turnings and iodine to 100 ml of methanol. The mixture was refluxed until the colour of iodine disappeared , then a further 600-800 ml of methanol added. The mixture was refluxed for 2 hours and the methanol distilled off . Dimethyl sulphoxide was dried with molecular sieves type **4A** , by passage through a column of fresh **4A** sieves , then distilled under reduced pressure. The distilled dimethyl sulphoxide was stored over molecular sieves type **4A** in an amber bottle . Pyridine was distilled and stored over potassium hydroxide pellets . Tetrahydrofuran was dried over sodium wire. The tetrahydrofuran was tested for peroxides using Merckoquant peroxide test strips and then distilled , under a flow of nitrogen , through a 30 cm vigreux column . All other solvents used were of **AnalaR** grade.

Analysis

Melting points

All melting points were recorded on a Reichert hotstage apparatus and are uncorrected.

NMR

^{1}H NMR spectra were recorded at 90 MHz on a Perkin–Elmer R32 spectrometer and at 200 MHz on Bruker AM and WP 200 SY instruments. The spectra were recorded in $CDCl_3$ solutions , unless otherwise stated. Chemical shifts are expressed in parts per million (δ) downfield from tetramethylsilane as internal reference .

Mass spectra

Mass spectra were run on a VG upgraded Kratos MS12 .

IR

IR spectra were recorded on Perkin–Elmer 580 and 983 spectrometers as KBr discs. The peaks of medium to high intensity are reported as ν_{max} in reciprocal centimetres .

Crystallographic Experimental

Data were collected on Enraf-Nonius CAD4 diffractometers at room temperature using Cu-Kα and Mo-Kα radiation.

Cell dimensions were derived from least-squares analysis of the setting angles of 25 reflections. During data collection two reference reflections were monitored periodically to check for any significant variation in intensity. The crystal structures were elucidated by the direct phasing program MITHRIL (Gilmore 1984). H atoms were located in difference Fourier synthesis. Full-matrix least-squares calculations were carried out on F with anisotropic thermal parameters for all non-H atoms and isotropic for H atoms. Fourier, least-squares,geometry and ORTEP calculations were performed with the GX package of programs (Mallinson & Muir, 1985). Scattering factors were obtained from International Tables for X-ray Crystallography

(1974).

For compound (41) the structure was solved by direct methods using SHELXS86 (Sheldrick 1986) and refined by full-matrix least-squares with SHELX76 (Sheldrick 1976).

Chapter 3

Condensations of 4-Nitroaniline with Formaldehyde and with Dimethylsulphoxide–Phosphorus Pentoxide

The difference in enthalpy between the chair and twist-boat conformers of cyclohexane is in excess of 20 $kJmol^{-1}$ (Hendrickson, 1961 ; Allinger , Hirsch, Miller, Tyminski & Van-Catledge, Wilberg & Boyd, 1972 ; Komornicki & McIvor Jr. 1973 ; Squillacote, Sheridan , Chapman & Anet, 1975) and at normal temperatures the twist-boat form is confined to substituted cyclohexanes in which syn-axial interactions in the chair form are relieved by conformational conversion to the twist-boat form. The differential is lowered appreciably by introduction of the carbonyl group and various derivatives of cyclohexane have been shown to exist in the twist-boat form (Eliel, Allinger, Angyal & Morrison, 1965). The twist-boat conformation is predominant in cyclohexane-1,4-dione (23) and has been studied in the crystal structures of derivatives of this compound (Groth & Hassel, 1964,1965 ; Mossel & Romers, 1964 ; Groth, 1968).

The conversion of cyclohexane to cyclohexanone involves the replacement of a tetrahedral sp^3 C atom by a trigonal sp^2 C atom and this raises the question of whether a twist-boat 1,3,5-triaryl-1,3,5-triazacyclohexane can be obtained if the N atoms have a coplanar, rather than a pyramidal , arrangement of bonds. Since the N atom in N,N-dimethylaniline (24) has a pyramidal bonding pattern (Cervellati, Borgo & Lister, 1982) whereas the corresponding atom in p-nitro-N,N-dimethylaniline (25) has a coplanar arrangement of bonds (Mak & Trotter, 1965.), the compound 1,3,5-tri-(p-nitrophenyl)1,3,5-triazacyclohexane (20) was thus selected for X-ray crystallographic analysis.

The condensation of 4-nitroaniline and formaldehyde gave, after 4 hours at room temperature, a yellow precipitate of the 2:1 adduct (21). The structure of the product (21) was established by its mirco-analytical data consistent with the molecular formula $C_{13}H_{12}N_4O_4$, and the melting point (229–230°) which is close to the literature value (230–232°) of the 2:1 condensation product (21) not the cyclic 3:3 product as expected. The IR spectrum of (21) shows the NH absorption at 3420 cm^{-1}. The NH signal in the ^1H NMR spectrum appeared as a singlet at δ 2.55 and the methylene protons as a sharp singlet at δ 4.7.

The reaction was carried out again changing the reaction conditions, firstly an increase in

reaction time and secondly an increase in reaction temperature but both of these reactions proved to be ineffective as both reactions again give the 2:1 condensation product (21). Compound (21) was recrystallised from acetone:ethanol (1:1) to give rod-like crystals. The surface of these rod-like crystals became cloudy when removed from the solvent and because of this factor the crystals were mounted in a sealed quartz glass capillary in the presence of a small amount of solvent mixture. This is done by placing a thin strip of filter paper soaked in the solvent mixture in the sealed end of the capillary and the crystal, mounted on a glass fibre, is sealed in the other end with glue. The rod-like crystals in the presence of solvent showed very weak diffraction with the diffractometer set to the highest possible energy settings 55 KV 28mA, insufficent data were collected to allow the crystal structure of this compound to be determined. In the absence of solvent the crystals gave no diffraction at all.

The possibilty existed that the insolubility of the 2:1 adduct (21) caused precipitation and prevented further condensation. In an attempt to hold (21) at least partly in solution 4-Nitroaniline and formalin were stirred in the more polar solvent tetrahydrofuran for 4 hours at room temperature in the presence of base (potassium hydroxide) but again the product was the 2:1 condensation adduct (21) and not the 3:3 cyclic product.

Since only the 2:1 adduct (21) could be obtained from the aniline- formaldehyde condensation, the cyclic trimer 1,3,5-tri-(4-nitrophenyl)-1,3,5-triazacyclohexane (20) was obtained by the method of Moffatt (Lerch & Moffatt, 1971) by adding phosphorus pentoxide to anhydrous dimethyl sulphoxide with stirring and cooling in ice. After 15 minutes 4-nitroaniline was added and the resulting clear solution was stirred for 48 hours during which time a solid separated. The mixture was diluted with dry methanol, filtered and the residue recrystallised from pyridine to give (20) as yellow needles with a melting point (279–281°) which was slighty lower than the literature value (286–287°). The mircoanalytical data of the crystals corresponds to the molecular formula $C_{21}H_{18}N_6O_6$ and had satisfactory spectroscopic characteristics. The aromatic proton resonances in ^1H NMR appeared at δ 7.21 and 8.09 and the ring methylene protons as a sharp singlet at δ 5.35. There are five distinct absorptions in the ^{13}C NMR at δ 138.88 and 153.35 due to aromatic quaternary carbons, 111.76 and 128.19 due to aromatic methine carbons and 51.02 due to aliphatic methylene carbons.

The insolubility of the compound (20) made its crystallisation from most common solvents very difficult. Slow crystallisation from pyridine, in a desiccator over silca gel for six weeks gave deep yellow prisms (22), with melting point (290–291°). The mircoanaylitical data allowed us to assign the prisms as a 1:1 solvate $C_{21}H_{18}N_6O_6$:C_6H_5N. The ^1H NMR absorptions were similar to those of (20) accompanied by pyridine resonances. The aromatic resonances appeared at δ 7.18 and 8.10, partly obscured by pyridine resonances at δ 7.36, 8.16 and 8.57. The ring methylene protons appeared as a singlet at δ 5.33.

The crystal faces of the inclusion compound became cloudy on standing suggesting slow

loss of included solvent.

A crystal (0.3 x 0.4 x 0.4 mm) of (22) was mounted on the Enraf-Nonius CAD4 diffractometer with Mo $\underline{K}\alpha$ radiation for crystal structure analysis. The cell dimensions were derived from the least-squares analysis of the setting of 25 independent reflections. 5022 reflections were surveyed in the range θ 1.5–25.0° and 3026 satisified the criterion $I \geq 2.5\sigma(I)$. Two reference reflections monitored periodically showed no significant variation in intensity over the period of collection.

The crystal structure was elucidated by the the direct phasing program MITHRIL (Gilmore 1984). After preliminary least-squares adjustments of the co-ordinates and anisotropic thermal parameters of the C, N and O atoms,the H atoms were located in difference Fourier synthesis and subsquently included in the least-squares calculations with isotropic thermal parameters. Initially all non-H atoms of the pyridine were treated as C ; inspection of the thermal parameters and location of the 5 H atoms unambiguously identifed the N atom and established that the pyridine molecule has an ordered orientation. Refinement of the occupation parameter for the pyridine molecule converged at 0.985(3) , indicating essentially complete occupation of the solvent site. The weighting scheme used was $w = 1/\sigma^2(|F_o|)$. The refinement converged at $R = 0.039$, $R_w = 0.050$.

The x-ray structure analysis showed that in the inclusion compound (22) between 1,3,5-Tri-(p-nitrophenyl)-1,3,5-triazazcyclohexane and pyridine, the triazacyclohexane exists in the twist-boat conformation and the unit cell contained four molecules of 1,3,5,tri(p-nitrophenyl)-1,3,5 triazacyclohexane and four molecules of pyridine. The pyridine molecules occupy open-ended spiral channels. In the pyridine molecule the N-C bonds , 1.300, 1.312(5)Å are a little shorter than the C-C bonds, 1.327–1.430(6), mean 1.368Å. Though the conformation departs a little from the ideal twist-boat form (**Table 5**), presumably in response to crystal packing requirements a substituted twist cyclohexane shows a similar skewing (**Table 5**). The twist-boat conformation of cyclohexane is flexible, there is pseudorotation through a sequence of twist-boat and boat forms with only small differ-

ences in energy and the torsional angles are easily altered (Hendricksen,1961 ; Pickett & Strauss, 1970 ; Graaf, Baas & Veen, 1980).

Although the finding of the twist-boat conformation was not unexpected, the argument about coplanar and pyramidal bonding patterns that led us to examine the p-nitrophenyl derivative must be regarded as dubious. 1,3,5- Triacetyl-1,3,5-triazacyclohexane (26) has coplanar bonds at the N atoms but the molecule adopts a chair conformation in the crystal (Choi, Santro & Marinkas, 1975). Moreover the N-C(aryl) bonds from the triazacyclohexane nucleus in the p-nitrophenyl compound are tilted at 21.2, 29.5 and 3.3(3)° to the CH_2-N-CH_2 planes at N(1), N(3) and N(5), respectively, so that the arrangement of N-C bonds is coplanar at only one of the N atoms, N(5). These out-of-plane angles are, nevertheless, smaller than the angles in other triazacyclohexanes, e.g. 32.6-48.5(4)° in the o- , m- , and p-fluorophenyl compounds(10), (11) and (12)(Bouchemma, McCabe & Sim, 1989).

The conformation found in a solid is not necessarily the predominant conformation of a set of molecules in solution or in the vapour phase. Unambiguous examples of packing forces influencing molecular conformation occur in polymorphic forms of crystals (Truter, 1983); two crystalline forms of humulene nitrosite (27), for example contain distinctly different conformers. (Khan, MacAlpine, Porte & Sim, 1983). Moreover incorporation of an inclusion compound may cause a molecule to adopt a conformation that differs from the minimum-energy conformation because of the host-guest interactions. (Freer, Gilmore, MacNicol & Wilson, 1980). The compound 3,3,6,6-tetramethyl-1,2,4,5- tetrathiane (28), for example crystallizes in the twist-boat conformation (Korp, Bernal, Watkins & Fronczek, 1981) whereas the inclusion compound it forms with hexakis (p-t-butylphenylthiomethyl) benzene (29) contains the chair conformation (MacNicol & Murphy, 1981) and calculations by molecular mechanics indicate that the chair form is less stable than the twist-boat form by 3kJ mol^{-1} (Allinger, Hickey & Kao, 1976). The adoption of the twist-boat conformation by the 1,3,5-tri-(p-nitrophenyl)-1,3,5-

triazacyclohexane molecule in the pyridine inclusion compound may represent another example of a response to host-guest interactions and crystal packing forces. An X-ray study of the unsolvated material would throw light on this matter but unfortunately the insolubility of compound (20) in most common solvents precluded its crystallisation from these solvents.

The exocyclic N-C(aryl) bonds from the triazacyclohexane ring have lengths 1.356, 1.382, and 1.400(2)Å, with the shortest bond associated with the smallest N-C(aryl) out-of-plane angle (3.3°) and the longest bond associated with the largest out-of-plane angle (29.5°). The correlation is connected with the quinonoid character of a p-nitroaniline fragment decreasing as the bonding pattern at N(amino) becomes more pyramidal. The N-C(aryl) bonds in the o- , m-, and p-fluorophenyl compounds are generally a little larger 1.398-1.427(3), mean 1.416Å, in agreement with the larger N-C(aryl) out-of-plane angles in these compounds. The N-CH_2 bond lengths in the triazacyclohexane nucleus 1.442-1.474(3), mean 1.461Å are very similar to these in the o-, m-, and p-fluorophenyl compounds, 1.443–1.479(4), mean 1.460Å (Bouchemma, McCabe & Sim, 1989). The CH_2-N-CH_2 angles are 110.6-112.5(2)° and the N-CH_2-N angles are 108.3-108.9(2)° whereas in the o-, m- and p-fluorophenyl compounds the corresponding angles are CH_2-N-CH_2 108.2-110.7(3)° and N-CH_2-N 110.5-113.0(3)°.

Atomic co-ordinates are listed in **Table 6**, molecular dimensions in **Tables 7 and 8**, and the torsion angles that define the conformation of the triazacyclohexane ring in **Table 5**. **Figure 8** drawn with ORTEP (Johnson, 1965.) illustrates the molecular geometry.The thermal ellipsoids of the C and N atoms are drawn at the 50% probability level and H atoms are represented by spheres of radius 0.1Å and **Figure 9** illustrates the packing of molecules in the unit cell, viewed along the b axis.

Ortep drawing of the inclusion compound between 1,3,5- Tri-(p-nitrophenyl)-1,3,5-triazazcyclohexane and pyridine (22) with the thermal ellipsoids of the C and N atoms are drawn at the 50% probability level and H atoms are represented by spheres of radius 0.1Å.

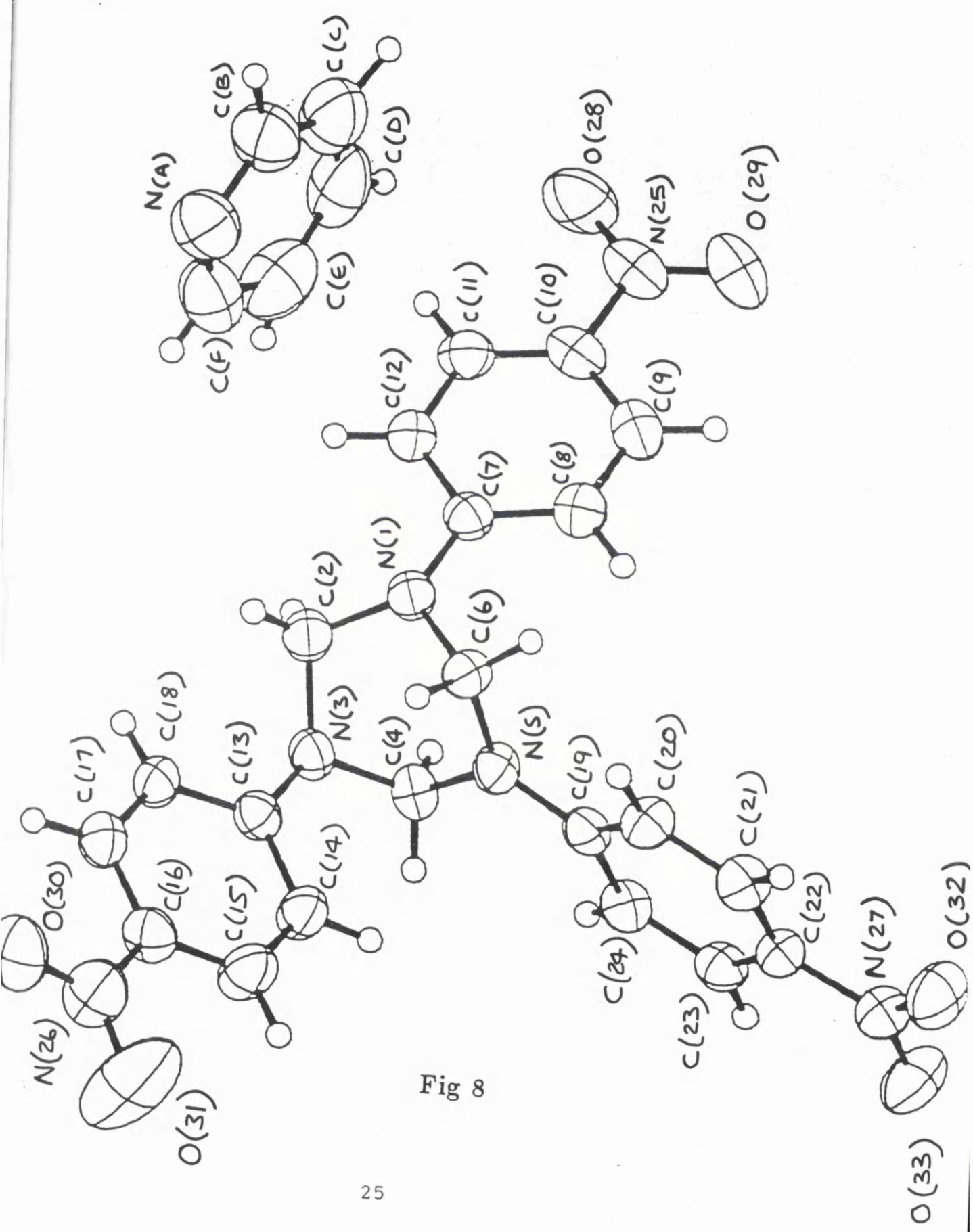


Fig 8

Crystal packing for the inclusion compound between 1,3,5-tri-(4-nitrophenyl)-1,3,5-triazacyclohexane and pyridine (22) viewed along the b axis.

Fig 9

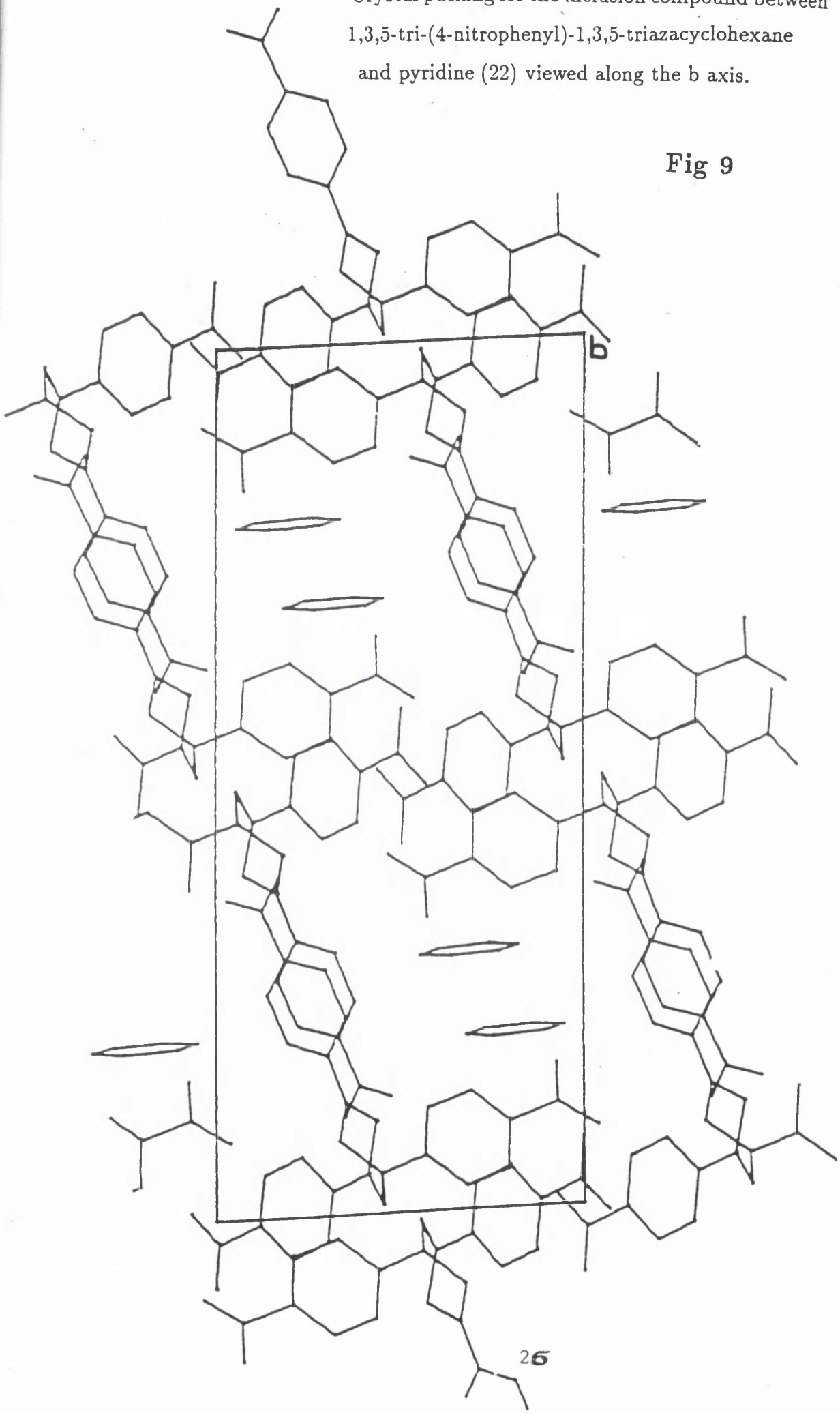


Table 5

Torsional angles (°) in twist-boat six-membered rings

Column **A** contains results for 1,3,5-tri-(p-nitrophenyl)-1,3,5- triazacyclohexane (22)

Column **B** contains results for 1,3-dihydroxymethyl-5-t- butylcyclohexane (30)

(Van Koningsveld, 1981)

Column **C** contains results for ideal twist-boat cyclohexane (Bucourt & Hainaut, 1965)

BOND	A	B	C
1-2	-25.3(2)	-20.2	-31
2-3	-41.3(2)	-38.8	-31
3-4	70.3(2)	62.2	65
4-5	-27.7(2)	-22.6	-31
5-6	-35.8(2)	-38.1	-31
6-1	66.0(2)	61.1	65

Several experiments were set up using compound (20) in an attempt to obtain crystals of inclusion compounds using solvents of similar size to pyridine under the same conditions. The results are given below in Table 9:

Table 9

Results of attempts to form other inclusion compounds.

SOLVENT	TIME	RESULTS
Benzene	8 weeks	no crystals
Toluene	6 weeks	no crystals
Collidine (Trimethylpyridine)	6 weeks	tiny needles
Lutidine (Dimethylpyridine)	6 weeks	no crystals

The tiny needle-like crystals obtained from collidine became cloudy about half an hour after removal from the solvent suggesting a loss of included solvent. The mircoanalytical data of the needles corresponded to the theoretical molecular formula $C_{21}H_{18}N_6O_6$ of unsolvated (20) (Found : C , 56.08 ; H , 4.12 ; N , 18.72.$\mathbf{C_{21}H_{18}N_6O_6}$ requires C , 56.00 ,H , 4.02 ; N , 18.65). It was noted, however that the crystal faces became fogged on standing and the crystals in that condition gave poor diffraction. As was found effective with pyridine, the crystals were mounted in a quartz glass capillary in the presence of a small amount of collidine but in this case they showed no diffraction.

Synthesis of 1,3,5–Tri–(4–nitrophenyl)–triazacyclohexane (20).

Phosphorus pentoxide (3.60 g) was added with stirring and cooling in ice to anhydrous dimethyl sulphoxide (15 ml).After 15 minutes, 4–nitroaniline (2.76 g , 20 mmol) was added and the resulting clear solution was stirred for 48 hours during which time a solid separated . The mixture was diluted with dry methanol , filtered and the residue (1.29 g : 43 %) recrystallised from pyridine to give (**16**) as yellow needles m.p. 279–280°C (lit. decomposition 286–287°C). These crystals were unsolvated (Found : C , 56.11 ; H , 4.11 ; N , 18.82. $\mathbf{C_{21}H_{18}N_6O_6}$ requires C , 56.00 ,H , 4.02 ; N , 18.65 %) ; m/z 300 , 150 , 120 , 104 , 92 and 77 ; λ_{max} (DMSO) 356 nm ; ν_{max} 1596 , 1509 , 1330 , 1233 , 950 and 835 cm^{-1} ; δ_H (d_6 - DMSO , 90 MHz) 5.35 (s , CH_2) , 7.21 and 8.09 (d , J = 9 Hz , Ar) in the area ratio of 1:1:1 ;δ_C (d_6 - DMSO , 50.3 MHz) 51.0 (CH_2) , 111.8 and 128.2 (Ar CH), 138.9 and 153.4 (Ar CN).

Synthesis of N,N–bis–(4–nitrophenyl)–diaminomethane (21).

4-Nitroaniline (2.07 g , 15 mmol) and formalin (3 ml) were stirred in dry tetrahydrofuran (30 ml) for 4 hours at room temperature . The yellow precipitate was filtered off and dried to yield (**17**) (0.95 g : 45 %) . Recrystallisation from ethanol : acetone (1 : 1) gave needles m.p. 229–230°C (lit. 230–232°C) (Found : C , 54.23 ; H , 4.13 ; N , 19.67. $\mathbf{C_{13}H_{12}N_4O_4}$ requires C , 54.16 ,H , 4.16 ; N , 19.44 %) ; m/z 150 , 138 , 120 , 108 , 92 , 77 and 65 ; ν_{max} 3420 (NH) , 1600 , 1528 , 1495 , 1320 , 1300 , 1260 , 1140 1120 , 1095 , 1040 , 830 and 755 cm^{-1} ;

Synthesis of 1,3,5–tri–(4–nitrophenyl)–1,3,5–triazacyclohexane :pyridine (1:1) inclusion compound (22).

Slow crystallisation of (**20**) (6 weeks) from anhydrous pyridine in a desiccator, over silca gel gave the 1:1 pyridine inclusion compound (22) as deep yellow prisms, m.p. (decomp.) 290–291° ; (Found C , 58.84 ; H , 4.10 ; N , 18.41. $\mathbf{C_{21}H_{18}N_6O_6.C_5H_5N}$ requires C , 58.97 ; H , 4.38 N , 18.52%) ; δ_H (d_6–DMSO) 5.33 (6H , s ; CH_2) , 7.18 (6H , d , J = 10 Hz ; Ar) and 8.10 (*ca.* 6H , d , J $\approx$ 10 Hz ; Ar) partly obscured by pyridine resonances at δ 7.36 (*ca.* 2H ,) , 8.16 (*ca.* 1H) and 8.57 (2H).

Crystallographic data of the (1:1) inclusion compound between 1,3,5–tri–(4–nitrophenyl)–1,3,5–triazacyclohexane:pyridine (22).

$C_{21}H_{18}N_6O_6.C_5H_5N$, $M_r = 529.57$, monoclinic , $P2_1/n$, $a = 9.848(3)$, $b = 10.636(3)$, $c = 23.216(4)$Å , $\beta = 93.110(20)°$, $V = 2428(2)$Å^3 , $Z = 4$, $D_x = 1.449$ g cm^{-3} , λ(Mo $K\alpha$) = 0.7107Å , $\mu = 0.12$ mm $^{-1}$, F (000) = 1104 , $T = 293$ K , $R = 0.039$ for 3026 independent reflections.

Crystal dimensions 0.3 x 0.4 x 0.4 mm . Enraf-Nonius CAD4 diffractometer , Mo $K\alpha$ radiation . Cell dimensions from setting angles of 25 independent reflections with θ 10.7–16.5° .Intensities of 5022 reflections surveyed in range θ 1.5–25.0° ; scan width 0.9° + 0.14° tan θ ; max. scan time 120 sec. ; h 0 → 11 , k 0 → 12 l -27 → 27 ; 309 pairs of equivalent reflections with $R_{int} = 0.024$; 3026 independent reflections with $I \geq 2.50(I)$. Two reference reflections monitored periodically showed no significant variation in intensity. No absorption correction. Structure determined by direct phasing using MITHRIL. H atoms located in difference Fourier synthesis. Full-matrix least-squares calculations on F with anisotropic thermal parameters for C , N and O atoms and isotropic for H atoms. Initially all non-H atoms of the pyridine were treated as C ; inspection of the thermal parameters and location of the 5 H atoms unambiguously identifed the N atom and established that the pyridine molecule has an ordered orientation. Refinement of the occupation parameter for the pyridine molecule converged at 0.985(3) , indicating essentially complete occupation of the solvent site. Least-squares convergance at R = 0.039 , $R_w = 0.050$, S 2.42 for 446 parameters , $\Delta/\sigma < 0.1$, $w = 1/\sigma^2$ ($|F_o|$). Final $\Delta\rho$ max 0.32 , min -0.16 eÅ^{-3}.

Chapter 4

Diaminomethanes from Condensations of Formaldehyde with 4-Acetyl-, 4-Metoxycarbonyl- and 2-Trifluoromethyl- Anilines

In Chapter 3, the formation of a 2:1 diaminomethane adduct (21) in the poly-condensation of formaldehyde and 4-nitroaniline was described. Such adducts have not been hitherto reported. In this Chapter evidance is presented for the generation of di-aminomethanes from condensations of formaldehyde with 4-acetyl-, 4-methoxycarbonyl- and 2-trifluoromethyl- anilines.

In an attempt to synthesise 1,3,5-tri-(4-acetylphenyl)-1,3,5-triazacyclohexane (31) 4-aminoacetophenone was stirred and heated for 2 hours in a oil bath (temperature slowly raised from 120°C to 130°) with paraformaldehyde in toluene and the azeotropic removal of water. The resulting precipitate when recrystallised from ethyl acetate gave (32) as very fine needles. The product of this reaction (32) was established by its mircoanalytical data consistent with the molecular formula $C_{17}H_{18}N_2O_2$ as the 2:1 condensation product not the cyclic 3:3 product as expected. The I.R. spectrum shows a strong absorption peak at 3360 cm^{-1} corresponding to N–H. The ^1H NMR gave four peaks ; a singlet at δ 2.41 due to CH_3 , a triplet at δ 4.82 due to CH_2 with a coupling constant 6Hz and also an AB system at δ 6.77 and 7.78 due to aromatic hydrogens with a coupling constant 8Hz.

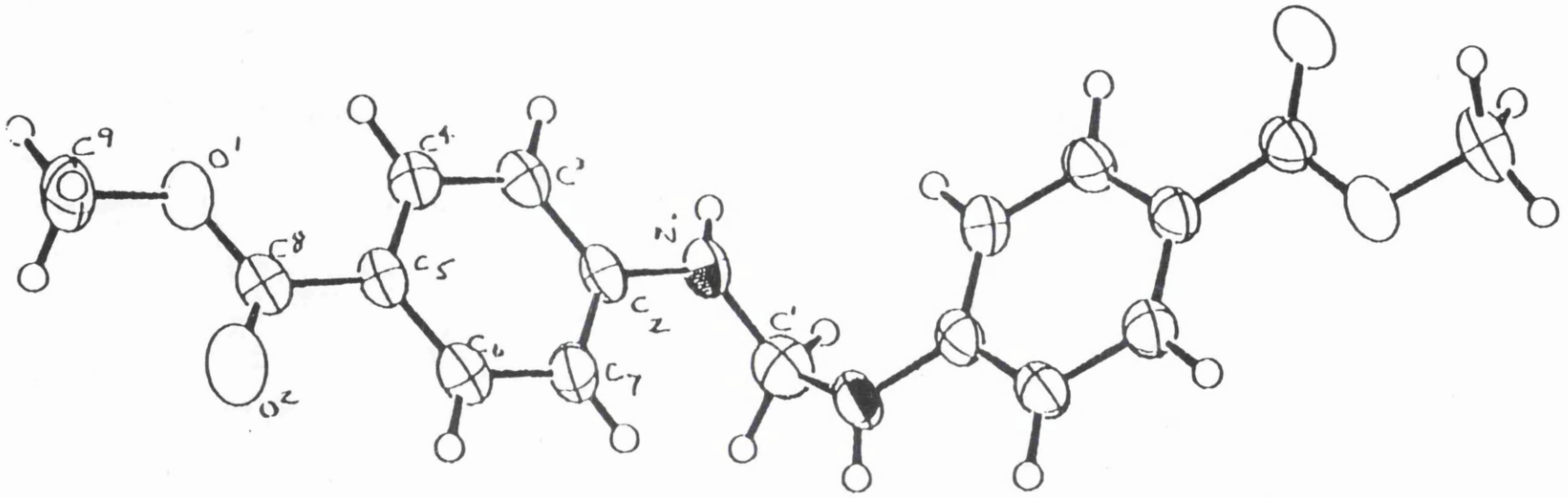
A series of crystallisation trials using a wide range of solvents and solvent mixtures have been carried out on this compound but so far have not resulted in obtaining a crystal of suitable size or diffracting power to enable us to solve the crystal structure of this compound.

In an attempt to synthesise 1,3,5-tri-(4-methoxycarbonylphenyl)-1,3,5-triazacyclohexane (33), methyl 4-aminobenzoate was stirred with formalin in dry tetrahydrofuran for 4 hours . The resulting fine white suspension was transfered to a centrifuge tube and spun for 2 hours and the supernatant tetrahydrofuran was drawn off with a Pasteur pipette and the residue taken up in hot ethyl acetate, **(34)** collected on cooling and when recrystallised from chloroform gave small hexagonal crystals . The product of this reaction (34) was established by its mircoanalytical data consistent with the molecular formula $C_{17}H_{18}N_2O_4$ as the 2:1 condensation product not the cyclic 3:3 product as expected.

A crystal (0.20 x 0.20 x 0.10 mm) of (34) was mounted on the Enraf-Nonius CAD4 diffractometer with Cu $\underline{K}\alpha$ radiation for crystal structure analysis. The cell dimensions were derived from the least-squares analysis of the setting of 25 independant reflections. 1644 reflections were surveyed in the range θ 1.0–70.0° and 1003 satisified the criterion I $\geq 2.5\sigma$(I).Two reference reflections monitored periodically showed no significant variation in intensity over the period of collection.

The crystal structure was elucidated by the the direct phasing program MITHRIL (Gilmore 1984). After preliminary least-squares adjustments of the co-ordinates and anisotropic thermal parameters of the C, N and O atoms,the H atoms were located in difference Fourier synthesis and subsquently included in the least-squares calculations with isotropic thermal parameters. The weighting scheme used was w = exp(FA $\sin^2\theta$ /λ^2)/ σ^2 (F_o). The calculations converged at R = 0.055 , R_w = 0.069. Atom C(1) lies on a crystallographic two-fold axis of symmetry. In the solid state N,N,–bis(4–methoxycarbonylphenyl)-diaminomethane (34) adopts a skewed conformation around both N–CH_2 bonds.The C(2)–N(1)–C(1)–N(1') torsion angle is -77.2°(3). and 63.3°(4). The bond angles in the chain linking the phenyl groups are distinctly greater than tetrahedral 124.2°(2) at N(1) , 113.9°(3) at C(1).

The N–CH_2 bond 1.450(4) is 0.08Å longer than the N–C(aryl) bonds 1.370(4). Atomic co-ordinates are listed in **(Table 10)** and molecular dimensions in **(Tables 11 and 12)**. **(Figure 10)** drawn with ORTEP (Johnson, 1965.) illustrates the molecular geometry.The thermal ellipsoids of the C and N atoms are drawn at the 50% probability level and H atoms are represented by spheres of radius 0.1Å.



Ortep drawing for N,N–bis(4–methoxycarbonylphenyl) diaminomethane thermal ellipsoids of the C, N and O atoms are drawn at the 50% probability level and H atoms are represented by spheres of radius 0.1Å

Fig 10

In an attempt to synthesise 1,3,5-tri-(2-trifluoromethylphenyl) -1,3,5-triazacyclohexane (35) paraformaldehyde was added portion wise to a solution of 2-aminobenzotrifluoride in benzene at 98°C over a period of 40 minutes with azeotropic removal of water. At the end of the addition a clear solution was obtained. It was kept for an additional 30 minutes at 98°C. Complete solvent removal under vacuum in an oil bath at 70°C gave an oil which solidified at ambient temperature to colourless needles, which were recrystallised from hexane to gave **(36)**. The product of this reaction (36) was established by its mircoanalytical data consistent with the molecular formula $C_{15}H_{12}F_6N_2$ as the 2:1 condensation product not the cyclic 3:3 product as expected. The mass spectrum gave the molecular ion at m/z = 333 and the I.R. spectrum showed a N–H stretching absorption at 3480 cm^{-1}. A crystal (0.25 x 0.37 x 0.55 mm) of (36) was mounted on the Enraf-Nonius CAD4 diffractometer with Mo $\underline{K}\alpha$ radiation for crystal structure analysis. The cell dimensions were derived from the least-squares analysis of the setting of 25 independent reflections. 3651 reflections were surveyed in the range θ 1.5–27.0° and 1604 satisified the criterion I $\geq 2.5\sigma(I)$.Two reference reflections monitored periodically showed no significant variation in intensity over the period of collection.

The crystal structure was elucidated by the the direct phasing program MITHRIL (Gilmore 1984). After preliminary least-squares adjustments of the co-ordinates and anisotropic thermal parameters of the C, N and F atoms,the H atoms were located in difference Fourier synthesis and subsquently included in the least-squares calculations with isotropic thermal parameters. The weighting scheme used was w = $1/\sigma^2(|F_o|)$. The calculations converged at R = 0.048 , R_w = 0.070. In the solid state N,N bis-(2-trifluoromethylphenyl)-diaminomethane (36) adopts a skewed conformation around both N–CH_2 bonds.The C(1A)–N(A)–C(8)–N(B) and C(1B)–N(B)–C(8)–N(A) torsion angles are 63.5°(4) and 63.3°(4).The N–CH_2 bond is rotated out of the plane of the adjacent phenyl ring to a small extent, the C(6A)–C(1A)–N(A)–C(8) and C(6B)–C(1B)–N(B)–C(8) torsion angles are 8.2°(4) and 6.5°(4). The bond angles in the chain linking the

phenyl groups are distinctly greater than tetrahedral 123.1°(4) at N(A) , 113.6°(3) at C(8) and 124.9°(4) at N(B).

The N–CH_2 bonds 1.459(6) and 1.439(6)Å are 0.07Å longer than the N–C(aryl) bonds 1.372(4) and 1.374(4)Å. Similar values for N–C(aryl) bonds have been observed in N,N-dialkylanilines with electron withdrawing substituents on the phenyl rings e.g. 1.362Å in 4-dimethylaminoazobenzene-2-carboxylic acid (37) (Moreiras, Solens, Solens, Mïravitlles, Germain & Declercq, 1980), 1.358Å in 4-dimethylamino-3-nitrocinnamic acid (38) (Huber, 1985), 1.368Å in N,N-di-n-propyl-2,6-dinitro 4 chloroaniline (39) (Towns, Brown, Teller & Giam, 1974).

In the trifluoromethyl groups the F–C–F angles are all smaller than tetrahedral 105.2°(4)–106.4°(4) mean 105.7° The C–F bond lengths are 1.318(5)–1.337(6) mean 1.330Å.

The short H...F distance between the H atoms on N(A) and N(B) and the F atoms of the adjacent CF_3 are H(NA)...F(1A) 2.36(3), H(NA)...F(2A) 2.35(4) , H(NB)...F(1B) 2.58(3) and H(NB)...F(2B) 2.31(3)Å. These contacts may represent intramolecular hydrogen bonding since there is no intermolecular hydrogen bonding.

Atomic co-ordinates are listed in **(Table 13)** and molecular dimensions in **(Tables 14 and 15)**.

(Figure 11) drawn with ORTEP (Johnson, 1965.) illustrates the molecular geometry.The thermal ellipsoids of the C and N atoms are drawn at the 50% probability level and H atoms are represented by spheres of radius 0.1Å.

Ortep drawing for N,N bis-(2-trifluoromethylphenyl)-diaminomethane (36) with the thermal ellipsoids of the C, F and N atoms are drawn at the 50% probability level and H atoms are represented by spheres of radius 0.1Å

FIG 11

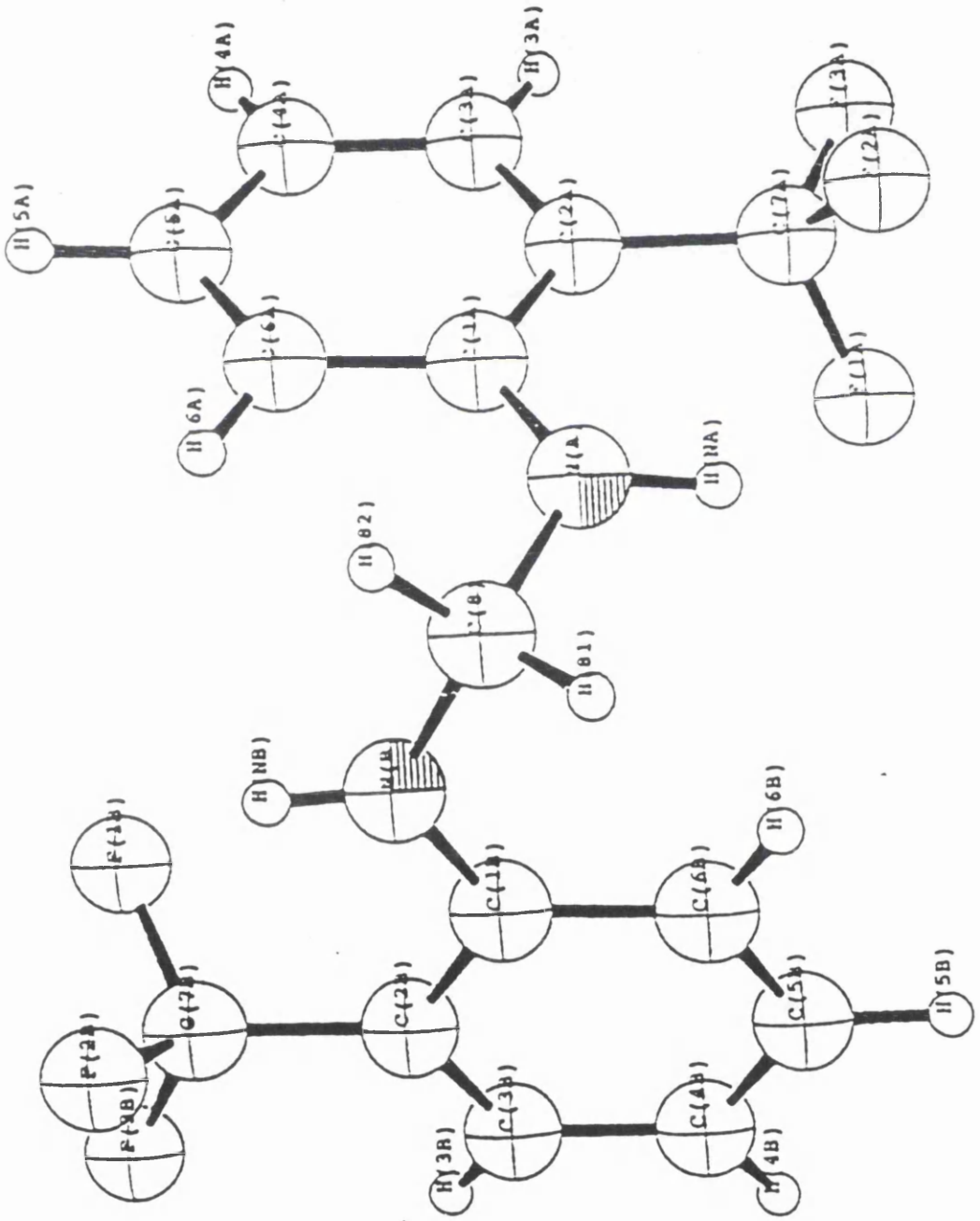
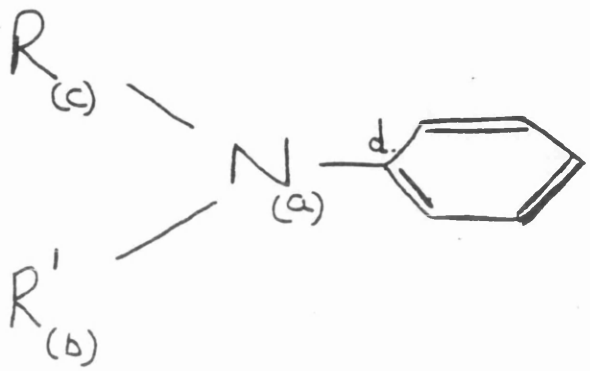


Table 16

Geometry comparisions between N,N-bis-(aryl)-diaminomethanes and N,N-dialkylanilines



In N,N-bis-(aryl)-diaminomethanes R'= H

	A	B	C	D	E
Bond a-d	1.362	1.358	1.368	1.372	1.370
Bond c-a	1.470	1.454	1.477	1.459	1.450
Bond b-a	1.460	1.455	1.452	0.94	0.90
∠bad	121.5	119.5	121.2	113.5	113.9
∠cad	119.7	123.1	120.0	123.1	124.2

Bond lengths in Å and angles in (°).

Column **A** 4-dimethylaminoazobenzene-2-carboxylic acid (37) (Moreiras, Solens, Solens, Miravitlles, Germain & Declercq, 1980)

Column **B** 4-dimethlyamino-3-nitrocinnamic acid (38) (Huber, 1985)

Column **C** N,N-di-n-propyl-2,6-dinitro 4 chloroaniline (39) (Towns, Brown, Teller & Giam, 1974).

Column **D** N,N-bis-(2-trifluoromethylphenyl)-diaminomethane (36)

Column **E** N,N-bis(4methoxycarbonylphenyl-)-diaminomethane. (34)

Synthesis of N,N–bis(4–acetylphenyl) diaminomethane (32).

4-Aminoacetophenone (2.70 g , 20 mmol)was stirred and heated for 2 hours (bath temperature slowly raised from 120°C to 130°) with paraformaldehyde (0.63 g , 21 mmol) in toluene (25 ml) with azeotropic removal of water , using a Dean and Stark apparatus. The resulting precipitate was filtered , washed with diethyl ether and recrystallised from ethyl acetate to yield **(32)** as very fine needles (2.49 g : 28 %) m.p. 198°C . (Found : C , 71.51 ; H , 6.60 ; N , 9.40. $\mathbf{C_{17}H_{18}N_2O_2}$ requires C , 72.32 ; H , 6.43 ; N , 9.92 %) ; m/z 147 , 135 , 132 , 120 , 104 , 92 and 77 ; ν_{max} 3360 , 1660 , 1590 , 1572 , 1530 , 1361 , 1321 , 1265 , 1173 , 1145 , 952 , 820 and 558 cm^{-1} ; δ_H (d_6 - Acetone , 200 MHz) 2.40 (s , CH_3) , 4.82 (t , CH_2) , 6.77 and 7.78 (m , Ar).

Synthesis of N,N–bis(4–methoxycarbonylphenyl) diaminomethane (34).

Methyl 4-aminobenzoate (7.56 g , 50mmol) was stirred with formalin (10 ml) in dry tetrahydrofuran (40 ml) for 4 hours . The resulting fine white suspension was transferred to a centrifuge tube and spun for 2 hours and the supernatant tetrahydrofuran was drawn

off with a Pasteur pipette and the residue dissolved in hot ethyl acetate, **(34)** collected on cooling and recrystallised from chloroform gave small hexagonal crystals . (Found : C , 64.95 ; H , 5.77 ; N , 8.75. $\mathbf{C_{17}H_{18}N_2O_4}$ requires C , 64.96 ,H , 5.77 ; N , 8.91 %) ; ν_{max} 3380 (NH) , 1695 , 1600 , 1530 , 1430 , 1320 , 1290 , 1260 , 1175 , 1110 and 770 cm^{-1} ;

Synthesis of N,N–bis–(2–trifluoromethylphenyl) diaminomethane (36).

To a solution of 2-aminobenzotrifluoride (3.23 g , 20 mmol) in benzene (20 ml) at 98°C paraformaldehyde (0.65 g , 22 mmol) was added portion wise over a period of 40 minutes with azeotropic removal of water , using a Dean and Stark apparatus. At the end of the addition a clear solution was obtained. It was kept for an additional 30 minutes at 98°C . Complete solvent removal under vacuum in an oil bath at 70°C gave an oil which solidified at ambient temperature to colourless needles , which were recrystallised from hexane to yield **(36)** (3.27 g : 94 %) m.p. 106–108°C. (Found : C , 53.80 ; H , 3.65 ; N , 8.30. $\mathbf{C_{15}H_{12}F_6N_2}$ requires C , 53.89 ,H , 3.62 ; N , 8.38 %) ; m/z 334 , 174 , 162 , 161 , and 145 ; ν_{max} 3480 (NH) , 3010 , 1612 , 1585 , 1470 , 1327 , 1270 , 1164 , 1105 and 1031 cm^{-1} ; δ_H 4.78 (t , 2H , NH) , 4.88 (d , 2H , CH_2) and 6.65–7.60 (m , 8H , Ar)

Crystallographic data of N,N–(4–methoxycarbonylphenyl) diaminomethane (34).

$C_{17}H_{18}N_2O_4$, M_r = 314.34 , monoclinic , $I2/c$, a = 14.0245(11) , b = 7.7864(6), c = 15.3572(18)Å , β = 113.00(1)° , V = 1543.7(3)Å^3 , Z = 4 , D_x = 1.352 g cm^{-3} , λ(Cu $K\alpha$) = 1.5418 Å , μ = 7.64 cm $^{-1}$, F (000) = 664 , T = 293 K , R = 0.055 for 1003 independent reflections.

Crystal dimensions 0.2 x 0.2 x 0.1 mm . Enraf-Nonius CAD4 diffractometer , Cu $K\alpha$ radiation . Cell dimensions from setting angles of 25 independent reflections with θ 10.0–33.8°. Intensities of 1644 reflections collected in range θ 1.0–70.0° ; scan width 0.9° + 0.14° tanθ ; max. scan time 120 sec. ; h 0 → 17 , k 0 → 9 l -18 → 18 ; 6 pairs of equivalent reflections with R_{int} = 0.017 ; 1003 independent reflections with $I \geq 2.50(I)$. Two reference reflections monitored periodically showed no significant variation in intensity. No absorption correction. Structure determined by direct phasing using MITHRIL. H atoms located in difference Fourier synthesis. Full-matrix least-squares calculations on F with anisotropic thermal parameters for C , N and O atoms and isotropic for H atoms. Least-squares convergance at R = 0.055 , R_w = 0.069 , S 3.43 for 168 parameters ,w = exp(FA sin$^2\theta$ /λ^2)/ σ^2 (F_o)

Crystallographic data of N,N–(2–trifluoromethylphenyl)–diaminomethane (36).

$C_{15}H_{12}N_2F_6$, M_r = 334.29 , monoclinic , $C2/c$, a = 20.018(3) , b = 4.942(2), c = 30.497(3)Å , β = 106.18(1)° , V = 2909(1)Å^3 , Z = 8 , D_x = 1.527 g cm^{-3} , λ(Mo $K\alpha$) = 0.71069 Å , μ = 0.16 mm $^{-1}$, F (000) = 1360 , T = 293 K , R = 0.048 for 1604 independent reflections.

Crystal dimensions 0.25 x 0.37 x 0.55 mm . Enraf-Nonius CAD4 diffractometer , Mo

$\underline{K}\alpha$ radiation . Cell dimensions from setting angles of 25 independent reflections with θ 12.07–20.0° .Intensities of 3651 reflections collected in range θ 1.5–27.0° ; scan width 0.8° + 0.25° tan θ ; max. scan time 100 sec. ; $\underline{h}$ 0 $\rightarrow$ 25 , $\underline{k}$ 0 $\rightarrow$ 6 $\underline{l}$ -39 $\rightarrow$ 39 ; 1604 independent reflections with $\underline{I} \geq 2.50(\underline{I})$. Two reference reflections monitored periodically showed no significant variation in intensity. Correction applied for Lorentz-polarisation effects, assuming an ideally imperfect monochromator crystal.Structure determined by direct phasing using MITHRIL.H atoms located in difference Fourier synthesis. Full-matrix least-squares calculations on $\underline{F}$ with anisotropic thermal parameters for C , N and F atoms and isotropic for H atoms. Least-squares convergance at $\underline{R} = 0.048$, $\underline{R}_w = 0.071$, $\underline{S}$ 3.29 for 257 parameters ,$\Delta/\sigma < 0.1$, $\underline{w} = 1/\sigma^2(|F_o|)$. Final $\Delta\rho$ max 0.20 , min -0.21 eÅ^{-3}.

Chapter 5

1,3,5-Triazacyclohexanes from Condensations of Formaldehyde with 4-Benzoyl-, 4-Cyano- and 3-Trifluoromethyl- Anilines

In previous Chapters, the anilines which condensed with formaldehyde to yield 2:1 diaminomethane adducts all bore electron-withdrwing substituents. This Chapter describes the formation of cyclic 3:3 adducts (1,3,5-triazacyclohexanes)from the poly-condensation of formaldehyde with anilines which also bear electron-withdrawing substituents.

1,3,5-Tri-(3-trifluoromethylphenyl)-1,3,5-triazacyclohexane (40) was synthesised by refluxing 3-aminobenzotrifluoride and paraformaldehyde in dried benzene in an oil bath at 90°C for 4 hours with the azeotropic removal of water. The remaining benzene was removed under vacuum and the resulting oil solidified on standing. The solid when recrystallised from petroleum ether(60-80°C) : hexane (1:1) gave (40) as colourless needles, melting point 68–70 °C which gave microanalytical figures consistent with the molecular formula $C_{24}H_{18}N_3F_9$.

A series of crystallisation trials using a wide range of solvents and solvent mixtures have been carried out on this compound but so far have not resulted in obtaining a crystal of suitable size or diffracting power to enable us to solve the crystal structure of this compound.

1,3,5-Tri-(4-cyanophenyl)-1,3,5-triazacyclohexane (41) was synthesised by stirring and heating for 2 hours (bath temperature slowly raised from 150°C to 160°C) 4-aminobenzonitrile with paraformaldehyde in toluene with azeotropic removal of water. The reaction solution was cooled and the resulting precipitate when recrystallised from ethyl acetate gave (41) as well formed needles, melting point 261°C , which gave microanalytical figures consistent with the molecular formula $C_{24}H_{18}N_6$. The ^{1}H NMR gave three peaks , a methylene singlet at δ 5.19 , and two doublets at δ 7.19 and 7.61 corresponding to the aromatic protons. The infra-red spectrum showed an absorption at 2225 cm^{-1} due to a carbon-nitrogen triple bond. In common with the other triazacyclohexyl compounds , the mass spectrum failed to show a molecular ion peak but gave an intense ion peak at $m/z = 130$ arising from the complete cleavage of the aminal ring.

The structure was solved by direct methods using SHELXS86 and refined by full-matrix

least-squares on the anisotropic thermal parameters for C and N atoms and isotropically for H atoms using SHELX76.The least-squares calculations converged at R = 0.137. The high R-factor for this compound is due to the quality of the data. There were a large number of weak reflections and there were only 2111 independent reflections with I $\geq$ 2.50(I). A low temperature data collection on this crystal in the future may give a better data set and allow refinement to carried out to give a lower R-factor.

From the imperfect data 1,3,5-Tri-(4-cyanophenyl)-1,3,5-triazacyclohexane (41) was seen to exist in the chair conformation Atomic co-ordinates are listed in **Table 17** and molecular dimensions in **Tables 18 and 19.**

1,3,5-tri-(4-benzoylphenyl)-1,3,5-triazacyclohexane (42) was synthesised by stirring and heating for 2 hours (bath temperature slowly raised from 160°C to 170°C) 4-Aminobenzophenone with paraformaldehyde in toluene with azeotropic removal of water using a Dean and Stark apparatus . The resulting precipitate when recrystallised from pyridine : hexane (1 : 1) gave (42). The microanalytical figures were consistent with molecular formula $C_{42}H_{33}N_3O_3$. The ^1H NMR showed a methylene signal at δ 5.20 , a doublet at δ 6.9 which is part of an AB system: with a coupling constant 9Hz and also a large multiplet at δ 7.6 incorporating the other doublet of the AB system both of these peaks are due to aromatic protons. The main peak in the I.R. spectrum is at 1640 cm^{-1} corresponding to C=O stretching frequency.

The recrystallisation of this compound from n-Hexane gave very thin clear needles.These needles were mounted in on the end of glass fibre but showed very weak diffraction when mounted on the CAD4 diffractometer thus proving not to be suitable for x-ray crystal structural analysis.

A further series of crystallisation trials using a wide range of solvents and solvent mixtures have been carried out on this compound but so far have not resulted in obtaining a crystal of suitable size or diffracting power to enable us to solve the crystal structure of this compound.

Synthesis of 1,3,5–tri(3–trifluormethylphenyl)–1,3,5–triazacyclohexane (40).

3-Aminobenzotrifluoride (4.83 g , 30 mmol) and paraformaldehyde (0.94 g , 31.3 mmol) were refluxed in dried benzene (30 ml) in an oil bath at 90°C for 4 hours with the azeotropic removal of water using an Dean and Stark apparatus . The remaining benzene was removed under vacuum and the resulting oil (4.93 g) solidified on standing .The solid was crystallised from petroleum ether (60-80°C) : hexane (1:1) to give (**40**) as colourless needles (3.5 g : 67 %) m.p. 68–70 °C .(Found : C , 55.39 ; H , 3.32 ; N , 8.10. $\mathbf{C_{24}H_{18}N_3F_9}$ requires C , 55.41 ; H , 3.49 ; N , 8.09 %) ; m/z 519 , 346 , 173 ; ν_{max} 1608 , 1491 , 1447 , 1441 , 1371 , 1341 , 1323 , 1226 , 1160 , 1112 , 999 , 948 , 801 and 558 cm^{-1} ; δ_H(200 MHz) 4.96 (s , 6H CH_2) , 7.2–7.45 (m , 12H , Ar).

Synthesis of 1,3,5–tri–(4–cyanophenyl)–1,3,5–triazacyclohexane (41).

4-Aminobenzonitrile (2.36 g , 20 mmol)was stirred and heated for 2 hours (bath temperature slowly raised from 150°C to 160°C) with paraformaldehyde (0.63 g , 21mmol) in toluene (25 ml) with azeotropic removal of water , using a Dean and Stark apparatus until condensation of water ceased . The reaction solution was cooled and the resulting precipitate was filtered , washed with diethyl ether and recrystallised from ethyl acetate to yield (**41**) (2.31 g : 29.6 %) m.p. 261° . (Found : C , 71.88 ; H , 4.77 ; N , 21.72. $\mathbf{C_{24}H_{18}N_6}$ requires C ,73.84 , H , 4.61 ; N , 21.53 %) ; m/z 130 , 129 , 118 , 102 , 91 and 76 ; ν_{max} 2225 , 1605 , 1510 , 1395 , 1320 , 1240 , 1170 , 935 , 825 and 545 cm^{-1} ; δ_H (d_6 - DMSO , 200 MHz) 5.19 (s , CH_2) , 7.19 and 7.61 (d , Ar).

Synthesis of 1,3,5–tri–(4–benzoylphenyl)–1,3,5–triazacyclohexane (42).

4-Aminobenzophenone (2.95 g , 15 mmol) was stirred and heated for 2 hours (bath temperature slowly raised from 160°C to 170°C) with paraformaldehyde (0.48 g , 16 mmol) in toluene (25 ml) with azeotropic removal of water using a Dean and Stark apparatus . The resulting precipitate was filtered , washed with diethyl ether, dried under vacuum and recrystallised from pyridine : hexane (1 : 1) to yield **(42)** (2.71 g : 29.0 %) m.p. 170°C .(Found : C , 79.85 ; H , 5.52 ; N , 6.89 . $\mathbf{C_{42}H_{33}N_3O_3}$ requires C , 80.38 ,H , 5.26 ; N , 6.69 %) ; m/z 209 , 197 , 132 , 120 , 105 and 77 ; ν_{max} 1645 , 1590 , 1575 , 1554 , 1516 , 1315 , 1285 , 1268 , 1150 , 838 , 744 and 700 cm^{-1} ; δ_H (d_6 - DMSO , 200 MHz) 5.20 (s , CH_2) , 6.90 and 7.60 (m , Ar).

Crystallographic data of

1,3,5–tri–(4–cyanophenyl)–1,3,5–triazacyclohexane (41).

$C_{24}H_{18}N_6$, M_r = 390 , monoclinic , $P2_1/c$, a = 25.5836(2) ,b = 20.2530(2), c = 7.8805(1)Å , V =4073(1)Å ^{3} ,Z = 8 , D_x = 1.273 g cm^{-3} , λ(Mo $K\alpha$) = 0.71069 Å , μ = 0.74 mm $^{-1}$, F (000) = 1632 , T = 293 K , R = 0.137 for 2111 independent reflections.

Crystal dimensions 0.10 x 0.15 x 0.20 mm . Enraf-Nonius CAD4 diffractometer, Mo $K\alpha$ radiation . Cell dimensions from setting angles of 25 independent reflections with θ 17.0–25.0° . Intensities of 2443 reflections surveyed in range θ 2.0–27.0° ; scan width 1.1° + 0.20° tan θ ; max. scan time 30 sec. ; h 0 → 8 , k 0 → 21 l -26 → 26 ; 2111 independent reflections with $I \geq 2.50(I)$. Two reference reflections monitored periodically showed no significant decline in intensity over the period of collection. The structure was solved by direct methods using SHELXS86 and refined by full-matrix least-squares on F with anisotropic thermal parameters for C and N atoms and isotropic for H atoms with SHELX76. Least-squares convergence at R = 0.137.

Chapter 6

1,3,5-Triazacyclohexanes from Condensation of Formaldehyde with 2- and 4-Methoxyanilines

The condensations of formaldehyde with 2-, 3- and 4-anisidines were undertaken to study the effect of bulky, electron-donating substituents on (i) the course of the poly-condensation reaction between formaldehyde and arylamines, and (ii) the conformation of the six-membered ring products (1,3,5-triazacyclohexanes) formed.

The ortho and para derivatives were prepared as described below but an attempt to prepare 1,3,5-tri-(3-methoxyphenyl)-1,3,5-triazacyclohexane (44) by stirring 3-anisidine in ethanol for 4 hours at room temperature with paraformaldehyde resulting in a black tar being formed from which the desired product could not be isolated. The reaction was carried out again changing the reaction parameters, firstly an increase in reaction time, secondly an increase in reaction temperature and a combination of both previous factors resulted again in forming a black tar like substance from which the product could not be isolated. In the future it might be worth attempting to synthesise 1,3,5-tri-(3-methoxyphenyl)-1,3,5-triazacyclohexane (44) by adding phosphorus pentoxide to anhydrous dimethyl sulphoxide with stirring and cooling in ice. After 15 minutes 3-anisidine added and the resulting clear solution stirred for 48 hours during which time the above product may be separated. This is the method that proved sucessful in synthesising the cyclic (3:3) compound (20) as described previously.

1,3,5-Tri-(2-methoxyphenyl)-1,3,5-triazacyclohexane (43) was synthesised by stirring 2-anisidine for 3 hours at 46° in an oil bath with paraformaldehyde in xylene containing 0.05g of sodium hydroxide. The xylene was removed under vacuum using an oil pump and the residue when recrystallised from acetone gave (43) as needles melting point 166-168°C which gave microanalytical figures consistent with the molecular formula $C_{24}H_{27}N_3O_3$. The ^1H NMR showed a sharp methoxy singlet at δ 3.82 and a methylene reasonace at δ 4.86. The mass spectra showed no molecular ion but the peak of highest mass at m/z = 135 was assigned to $[\ CH_3OC_6H_4NCH_2\ ]^+$ (M/3).

A crystal (0.17 x 0.33 x 0.50 mm) of (43) was mounted on the Enraf-Nonius CAD4 diffractometer with Mo $\underline{K}\alpha$ radiation for crystal structure analysis. The cell dimensions

were derived from the least-squares analysis of the setting of 25 independent reflections. 5280 reflections were surveyed in the range θ 1.5–28.5° and 3691 satisified the criterion I $\geq 2.5\sigma(I)$.Two reference reflections monitored periodically showed 2% decline in intensity over the period of collection.

The crystal structure was solved by the the direct phasing program MITHRIL (Gilmore 1984). After preliminary least-squares adjustments of the co-ordinates and anisotropic thermal parameters of the C, N and O atoms,the H atoms were located in difference Fourier synthesis and subsquently included in the least-squares calculations with isotropic thermal parameters. The weighting scheme used was $w = 1/\sigma^2(|F_o|)$. The calculations converged at $R = 0.038$, $R_w = 0.050$.

1,3,5-tri-(4-methoxyphenyl)-1,3,5-triazacyclohexane (45) was synthesised by adding formalin with stirring to a solution of 4–anisidine in ethanol at room temperature for one hour . The resulting precipitate when recrystallised from ethanol gave (45) as needles melting point 133°C which gave microanalytical figures consistent with the molecular formula $C_{24}H_{27}N_3O_3$. The ^1H NMR showed a sharp methoxy singlet at δ 3.82 and methylene reasonace at δ 4.66. The aromatic resonances appear as an AB double doublet (J= 9Hz). The mass spectra showed no molecular ion but the peak of highest mass at m/z = 135 was assigned to [$CH_3OC_6H_4NCH_2$]$^+$ (M/3).

A crystal (0.10 x 0.35 x 0.35 mm) of (45) was mounted on the Enraf-Nonius CAD4 diffractometer with Cu $\underline{K}\alpha$ radiation for crystal structure analysis. The cell dimensions were derived from the least-squares analysis of the setting of 25 independent reflections. 2443 reflections were surveyed in the range θ 2.0–72.0° and 2111 satisified the criterion I $\geq 2.5\sigma(I)$. Two reference reflections monitored periodically showed 1% decline in intensity over the period of collection.

The crystal structure was elucidated by the the direct phasing program MITHRIL (Gilmore 1984). After preliminary least-squares adjustments of the co-ordinates and anisotropic thermal parameters of the C, N and O atoms,the H atoms were located in dif-

ference Fourier synthesis and subsquently included in the least-squares calculations with isotropic thermal parameters. The weighting scheme used was w = $1/\sigma^2(|F_o|)$. The calculations converged at R = 0.027 , R_w = 0.036.

Figures 12 and 13 drawn with ORTEP (Johnson 1965), show the molecular structures. Conformational details of the molecules are listed in **Tables 20-25** .Both molecules adopt the *aae* chair conformation, with diaxial repulsion between aryl groups preferred to that of lone pairs of electrons. A like result was obtained for 1,3,5-triphenyl-1,3,5-triazacyclohexane (46) (Giumanini,Verado, Randaccio, Bresciani-Pahar & Traldi, 1985).The alternative *eea* chair conformation has been found in the crystal structure of 1,3,5- tricyclohexyl-1,3,5-triazacyclohexane (47), in accord with the greater steric requirements of the cyclohexyl group (Bouchemma, McCabe & Sim 1988).

The N atoms have pyramidal geometery with the N–C (aryl) bonds inclined at 30.8–44.9(2)° to their CH_2–N–CH_2 planes. For comparison , microwave spectroscopy studies indicate that the out-of-plane angle of the N–C (aryl) bond is 37.5–42.2° in aniline (Larsen , Hansen & Nicolaisin 1976 : Lister, Tyler , Hog & Larsen 1974.), 27.0 ° in N,N-dimethylaniline (24) (Cervellati, Borgo & Lister 1982) and 46.4° in p-fluoroaniline (48) (Hastie, Lister, McNeil & Tyler 1970). The N atoms in aliphatic amines are associated with larger out-of- plane angles than N atoms in aromatic amines and the N–C out-of-plane angles in 1,3,5-tricyclohexyl-1,3,5-triazacyclohexane (47) are 46.1–52.2(2)° (Bouchemma, McCabe & Sim 1988). The out-of-plane angles in a tetrahedral arrangement of bonds is 54.7° and the N–C(axial) bonds in the o-OMe and p-OMe compounds are consequently bent outwards by 15-24° from the ideal chair conformer , reducing the interactions between the axial aryl groups.

The orientations of the aryl groups about the N–C(aryl) bonds reflect the increased steric requirements when the aryl group is changed from p- to o- methoxyphenyl.

The angle (**Table 26**) for the p-OMe is in the range 62.4- 63.6(3)°, indicating that the dihedral angle between the N lone-pair orbital and the aromatic π -orbitals is ca 28-26°,

whereas in the o-OMe compound is 32.8 - 40.0° and the lone-pair/π-orbital dihedral angle is increased to 57-50 . In the absence of steric effects the lone-pair/π-orbital dihedral angle would be expected to be 0° to provide maximum overlap.

The N atoms deviate from the phenyl planes by 0.036–0.160(3)Å and the O atoms deviate by 0.004–0.079(3)Å giving out-of-plane angles of 1.4–6.3(3), mean 4.4° for the C(aryl)–N bonds and 0.2–3.3(3) , mean 1.1° for the C(aryl)–O bonds. MO calculations for aniline give a non-planar equilibrum geometry with the C(aryl)–N bond inclined at 2.4° to the aromatic plane (Niu & Boggs, 1984).

The packing of the o-substituted molecules in the unit cell is rather more compact than that of the p-substituted molecules, since V/Z for the o-OMe compound is 520Å and V/Z for the p-OMe compound is 539Å. Similar results were obtained for the o- and p-fluorophenyl and the o- and p- chlorophenyl compounds.

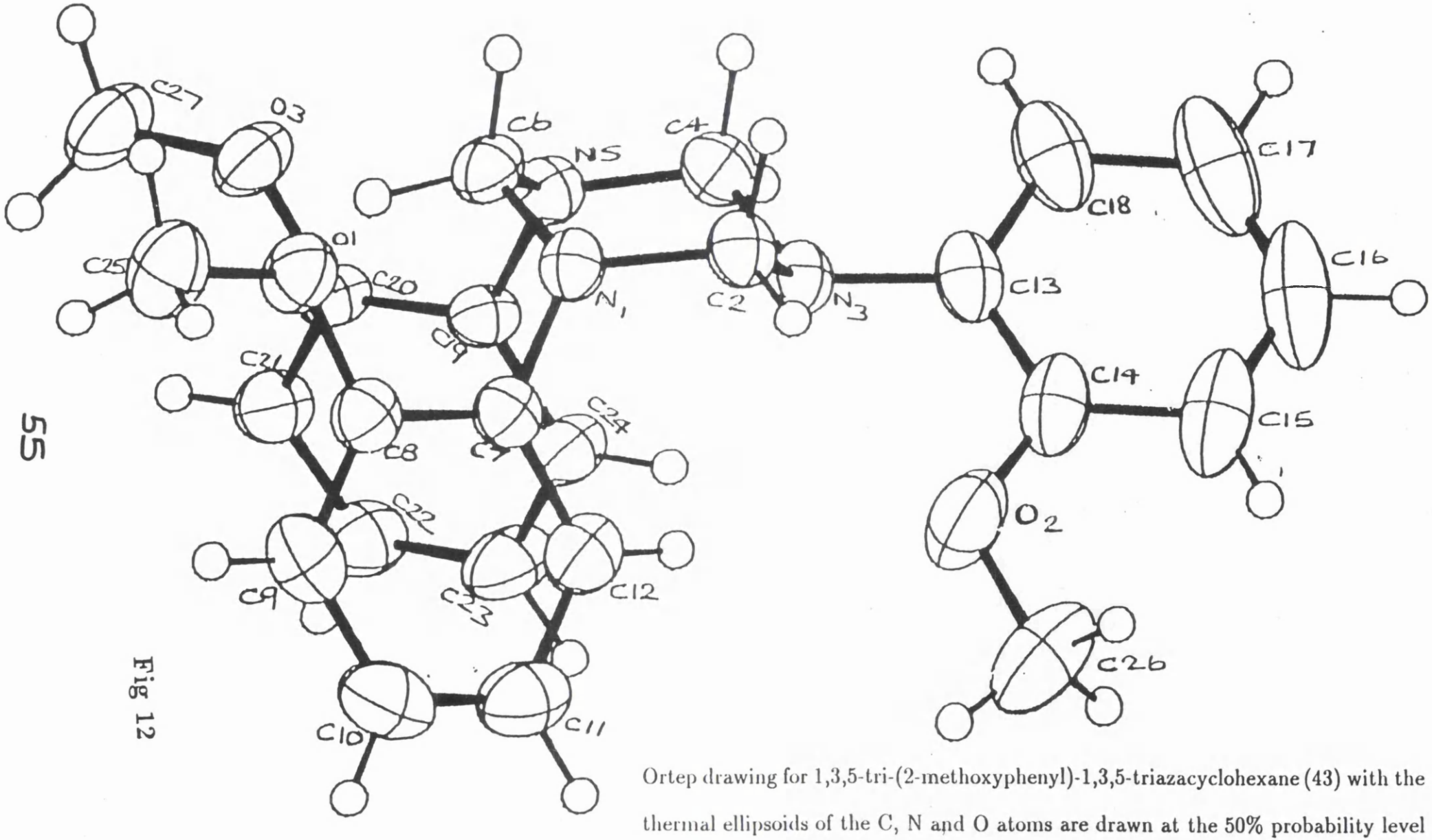


Fig 12

Ortep drawing for 1,3,5-tri-(2-methoxyphenyl)-1,3,5-triazacyclohexane (43) with the thermal ellipsoids of the C, N and O atoms are drawn at the 50% probability level and H atoms are represented by spheres of radius 0.1Å

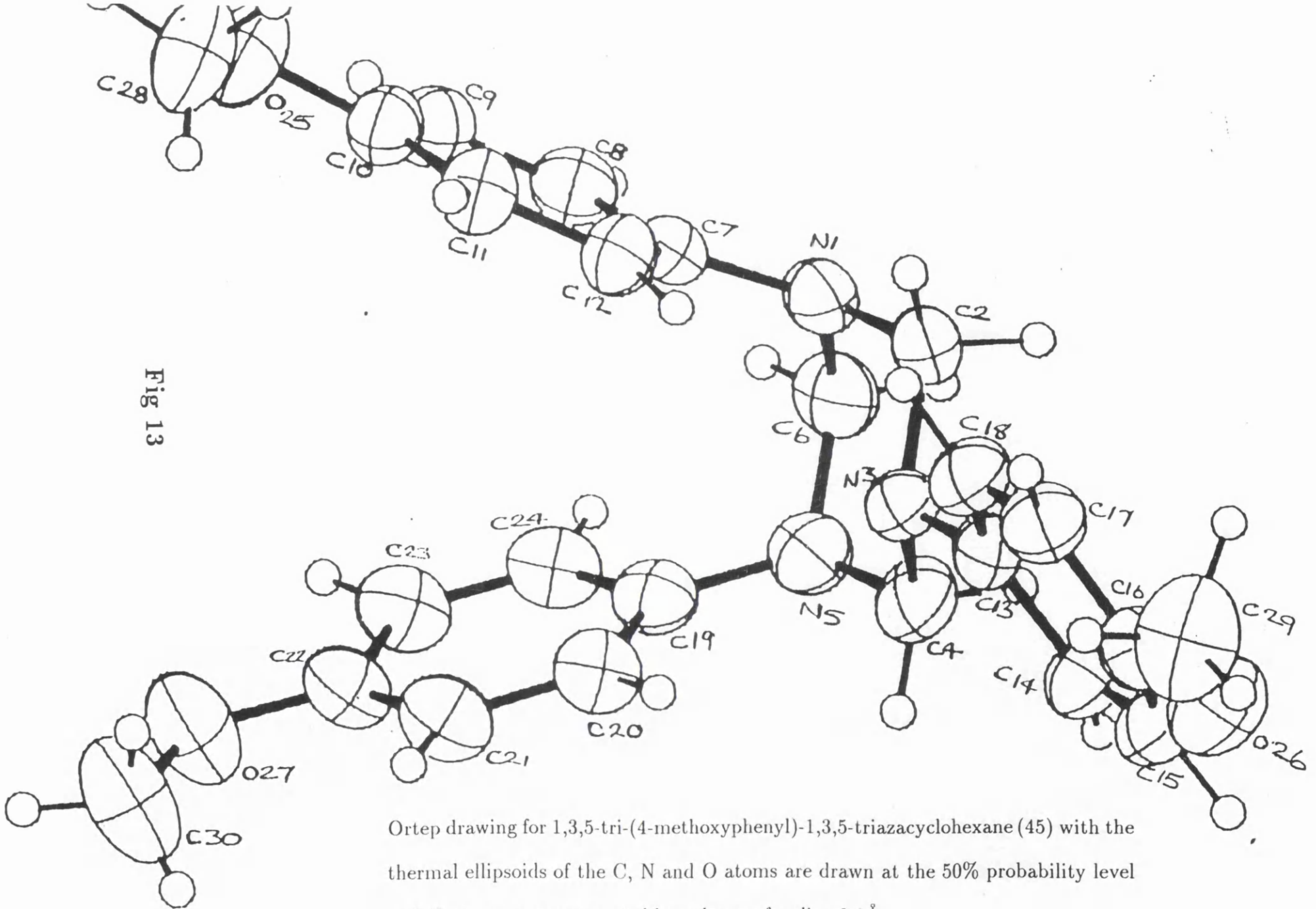
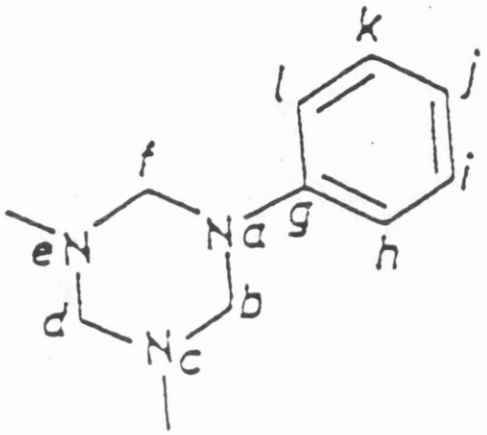


Fig 13

Ortep drawing for 1,3,5-tri-(4-methoxyphenyl)-1,3,5-triazacyclohexane (45) with the thermal ellipsoids of the C, N and O atoms are drawn at the 50% probability level and H atoms are represented by spheres of radius 0.1Å

Table 26

Conformational details of the *o* and *p*-methoxy compounds (43 and 45)



θ is the angle between planes **dagj** and **aghijkl**

γ is the angle between bond **a–g** and plane **fab**

ζ is the angle between bond **a–g** and plane **ghijkl**

		θ	γ	ζ
o-OMe	N(3) equatorial	40.0(3)	44.9(3)	3.7(3)
(43)	N(1) axial	38.4	30.8	5.3
	N(5) axial	3.28	35.5	6.0
p-OMe	N(3) equatorial	63.3(3)	43.1(3)	3.5(3)
(45)	N(1) axial	63.6	35.0	6.5
	N(5) axial	62.4	39.5	1.4

Synthesis of 1,3,5–tri–(2–methoxyphenyl)–1,3,5–triazacyclohexane (43).

2-Anisidine (6.16 g , 50 mmol) was stirred for 3 hours at 46° in an oil bath with paraformaldehyde (1.58 , 52.5 mmol) in xylene(30 ml) containing 0.05g of sodium hydroxide . The xylene was removed under vacuum using an oil pump and the residue recrystallised from acetone to give (**43**)(5.94 g : 88 %) as needles m.p. 166-168°C . (Found : C , 71.17 ; H , 6.79 ; N , 10.35. $\mathbf{C_{24}H_{27}N_3O_3}$ requires C , 71.08 , H , 6.71 ; N , 10.36 %) ; m/z 135 , 134 , 121 , 107 , 92 and 77 ; ν_{max} (KBr) 3000 , 2838 , 1595 , 1500 , 1465 , 1454 , 1196 1175 , 1112 , 1030 , 1000 , 940 and 770 cm^{-1} ; δ_H 3.82 (s , 9H CH_3) , 4.86 (6H , s , CH_2) , 6.67-7.00 (12H , m , Ar) .

Synthesis of 1,3,5–tri–(4–methoxyphenyl)–1,3,5–triazacyclohexane (45).

Formalin (8 ml) was added with stirring to a solution of 4–anisidine (6.18 g , 50 mmol) in ethanol (20 ml) at room temperature and stirring continued for one hour . The resulting precipitate was filtered and dried to yield (**45**) (4.88 g : 72 %) which recrystallised from ethanol to give needles m.p. 133°C (Found : C , 70.99 ; H , 6.85 ; N , 10.25 . $\mathbf{C_{24}H_{27}N_3O_3}$ requires C , 71.08 , H , 6.71 ; N , 10.36 %) ; m/z 135 , 134 , 107 and 92 ; ν_{max} 2957 , 2835 , 1510 , 1246 , 1185 , 1157 , 1036 , 987 , 940 and 825 cm^{-1} ; δ_H 3.72 (9H , s , CH_3) , 4.66 (6H , s , CH_2) and 7.00 (6H , d , Ar) .

Crystallographic data of

1,3,5–tri–(2–methoxyphenyl)–1,3,5–triazacyclohexane (43).

$\mathbf{C_{24}H_{27}N_3O_3}$, M_r = 405.53 , triclinic , $\underline{P}1$, $\underline{a}$ = 8.582(2) ,$\underline{b}$ =8.996(2), $\underline{c}$ = 15.357(3)Å ,

$\alpha = 94.90(1)$, $\beta = 93.27(1)$, $\gamma = 117.59(1)°$, $\underline{V}$ =1040Å^3 , $\underline{Z} = 2$, $\underline{D_x} = 1.29$ g cm^{-3} , λ(Mo $\underline{K}\alpha$) = 0.71069 Å , $\mu = 0.09$ mm $^{-1}$, $\underline{F}$ (000) = 432 , $\underline{T}$ = 293 K , $\underline{R}$ = 0.038 for 3691 independent reflections.

Crystal dimensions 0.17 x 0.33 x 0.50 mm . Enraf-Nonius CAD4 diffractometer , Mo $\underline{K}\alpha$ radiation . Cell dimensions from setting angles of 25 independent reflections with θ 12.00–17.0° .Intensities of 5280 reflections surveyed in range θ 1.5–28.5° ; scan width 0.9° + 0.35° tan θ ; max. scan time 120 sec. ; $\underline{h}$ 0 → 11 , $\underline{k}$ -12 → -12 $\underline{l}$ -20 → 20 ; 3691 independent reflections with $\underline{I} \geq 2.50\sigma$(I). Two reference reflections monitored periodically showed a decline of 2% over the period of collection. Correction applied for Lorentz-polarisation effects, assuming an ideally imperfect monochromator crystal.Structure determined by direct phasing using MITHRIL.H atoms located in difference Fourier synthesis. Full-matrix least-squares calculations on $\underline{F}$ with anisotropic thermal parameters for C and N atoms and isotropic for H atoms. Least-squares convergance at $\underline{R} = 0.038$, $\underline{R_w} = 0.050$, $\underline{S}$ 2.23 for 380 parameters ,$\Delta/\sigma < 0.3$, $\underline{w} = 1/\sigma^2(|F_o|)$. Final $\Delta\rho$ max 0.19 , min -0.21 eÅ^{-3}.

Crystallographic data of

1,3,5–tri–(4–methoxyphenyl)–1,3,5–triazacyclohexane (45).

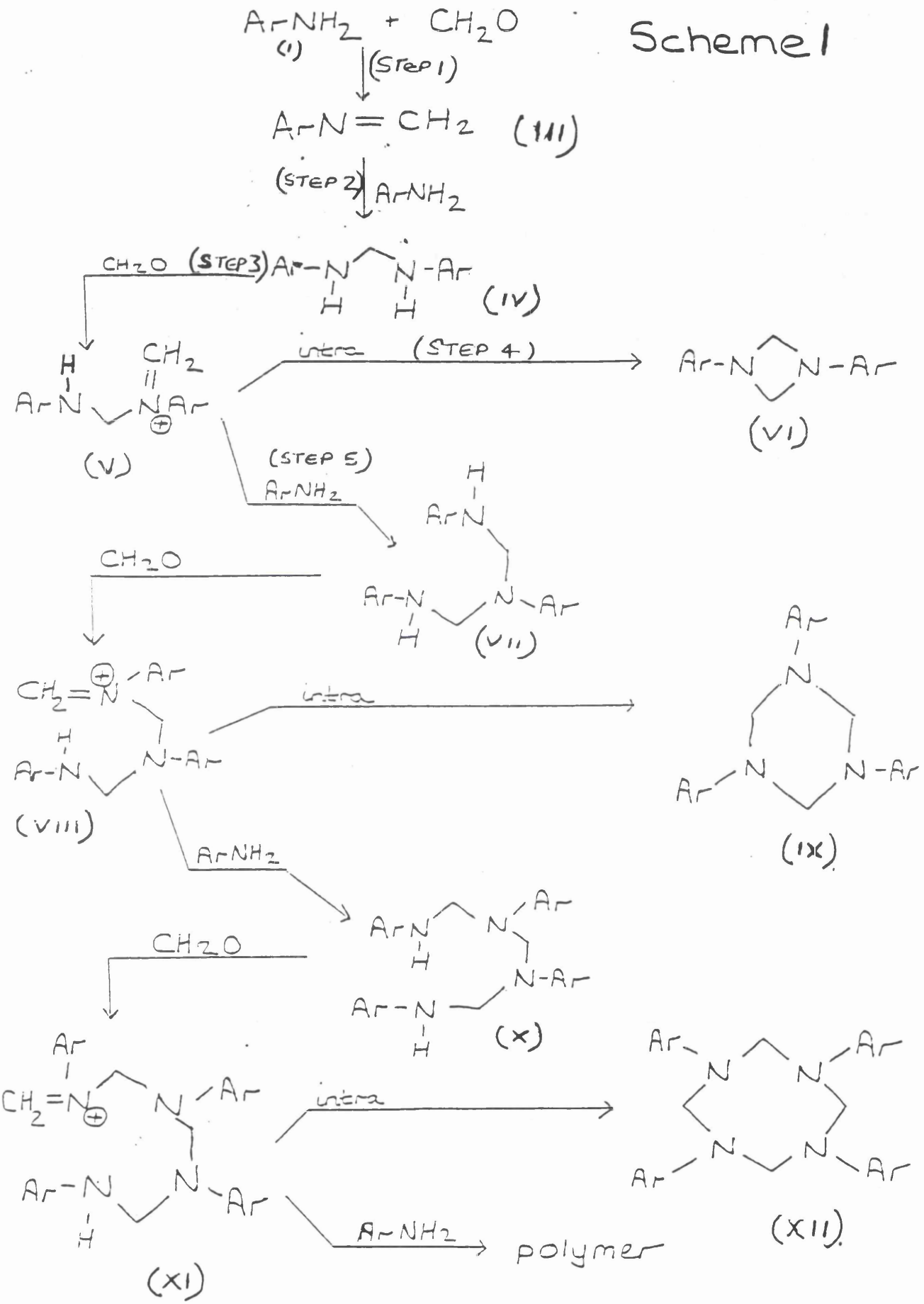
$C_{24}H_{27}N_3O_3$, M_r = 405.53 , orthorhombic , $\underline{P}ca2_1$, $\underline{a}$ = 15.518(2) ,$\underline{b}$ =16.427(2), $\underline{c}$ = 8.460(1)Å , $\underline{V}$ =2157(1)Å^3 , $\underline{Z}$ = 4 , $\underline{D_x}$ = 1.25 g cm^{-3} , λ(Cu $\underline{K}\alpha$) = 01.5418 Å , μ = 0.68 mm $^{-1}$, $\underline{F}$ (000) = 864 , $\underline{T}$ = 293 K , $\underline{R}$ = 0.027 for 2111 independent reflections.

Crystal dimensions 0.10 x 0.35 x 0.35 mm . Enraf-Nonius CAD4 diffractometer , Cu $\underline{K}\alpha$ radiation . Cell dimensions from setting angles of 25 independent reflections with θ 17.00–25.0° .Intensities of 2443 reflections surveyed in range θ 2.0–72.0° ; scan width 1.1° + 0.20° tan θ ; max. scan time 120 sec. ; $\underline{h}$ 0 → 19 , $\underline{k}$ 0 → 20 $\underline{l}$ 0 → 10 ; 2111 independent reflections with $\underline{I} \geq 2.50(\sigma$(I). Two reference reflections monitored periodically showed a decline of 1% over the period of collection. Correction applied for Lorentz-polarisation

effects, assuming an ideally imperfect monochromator crystal.Structure determined by direct phasing using MITHRIL.H atoms located in difference Fourier synthesis. Full-matrix least-squares calculations on $\underline{F}$ with anisotropic thermal parameters for C and N atoms and isotropic for H atoms. Least-squares convergance at $\underline{R} = 0.027$, $\underline{R_w} = 0.036$, $\underline{S}$ 1.88 for 379 parameters ,$\Delta/\sigma < 0.3$, $\underline{w} = 1/\sigma^2(|F_o|)$. Final $\Delta\rho$ max 0.11 , min -0.11 $eÅ^{-3}$.

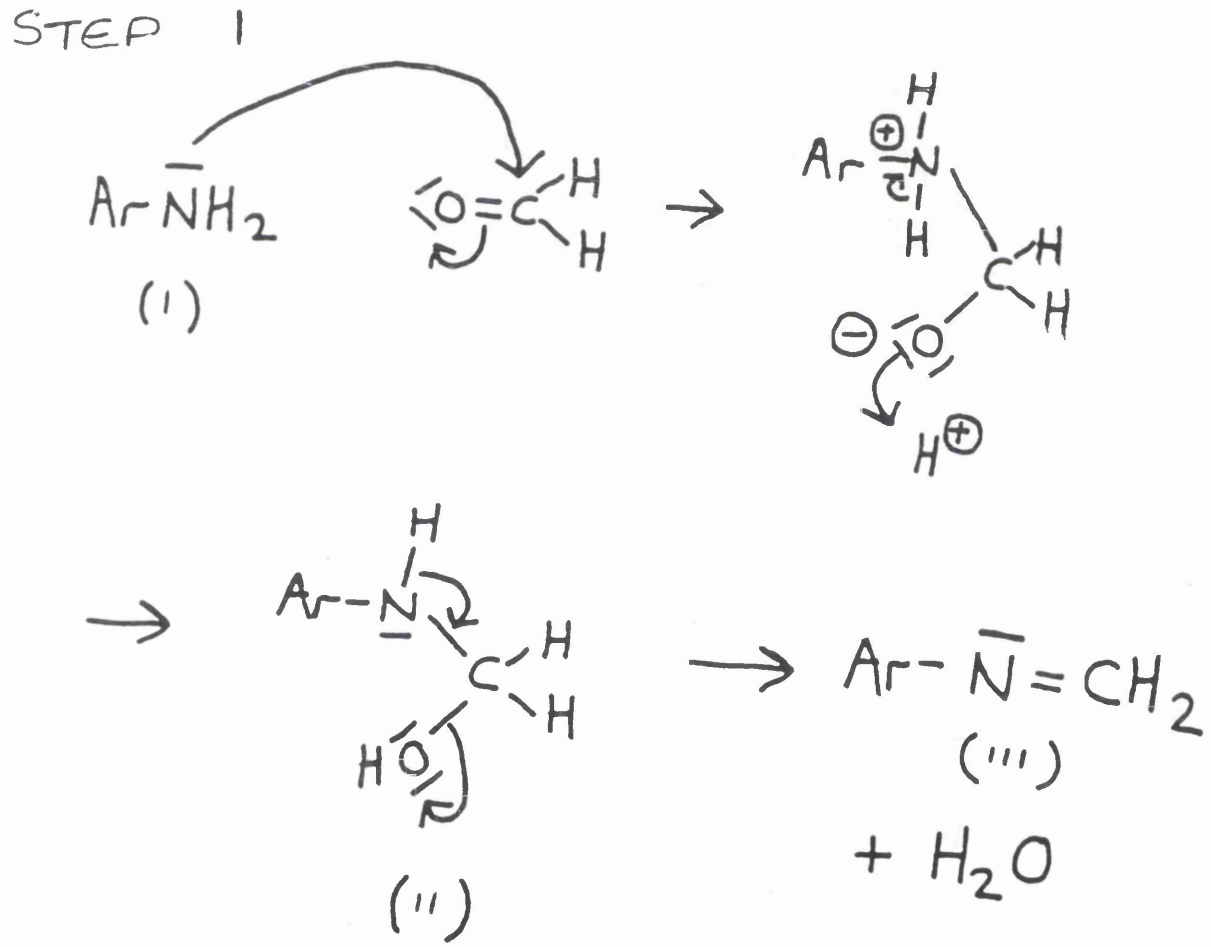
Conclusion

Scheme 1


ArNH2 + CH2O
(I)
(STEP 1)
Ar-N=CH2 (III)
(STEP 2) ArNH2
CH2O (STEP 3)
(IV)
intra (STEP 4)
(V)
(VI)
(STEP 5)
ArNH2
(VII)
CH2O
intra
(VIII)
(IX)
ArNH2
(X)
CH2O
intra
(XI)
(XII)
ArNH2
polymer

A stepwise spectulative mechanism for the poly-condensation of formaldehyde with arylamines is proposed in Scheme 1. This proposal is based on verification of the structures of certain of the poly-condensed products e.g. the 2:2 and 3:3 adducts described in this thesis and in that of A. Bouchemma and the 1:1, cyclic 2:2 and cyclic 4:4 adducts described elsewhere.

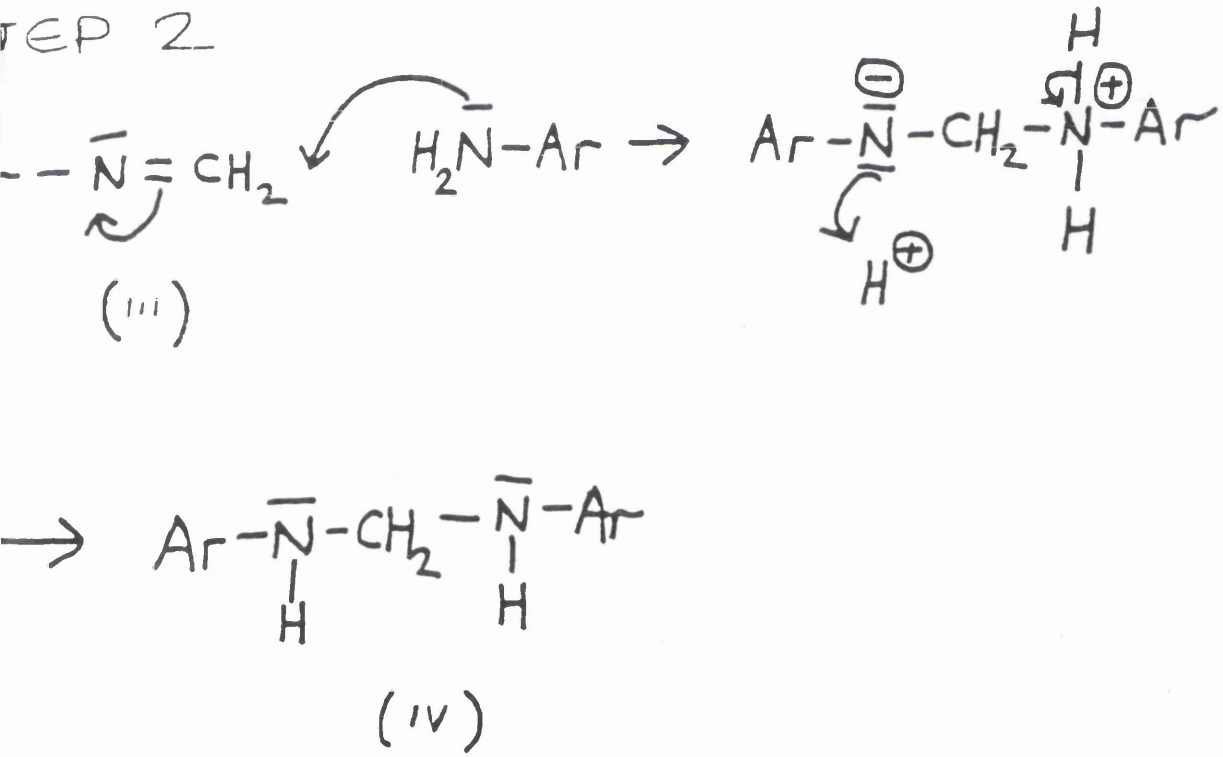
In Step 1 of Scheme 1, the nucleophlic attack of the amine nitrogen lone pair of (i) on the formaldehyde carbonyl carbon (addition) followed by proton transfer and elimination of water from the hydroxyamine (ii) produces the imines (iii) as detailed in Scheme 2.



Scheme 2

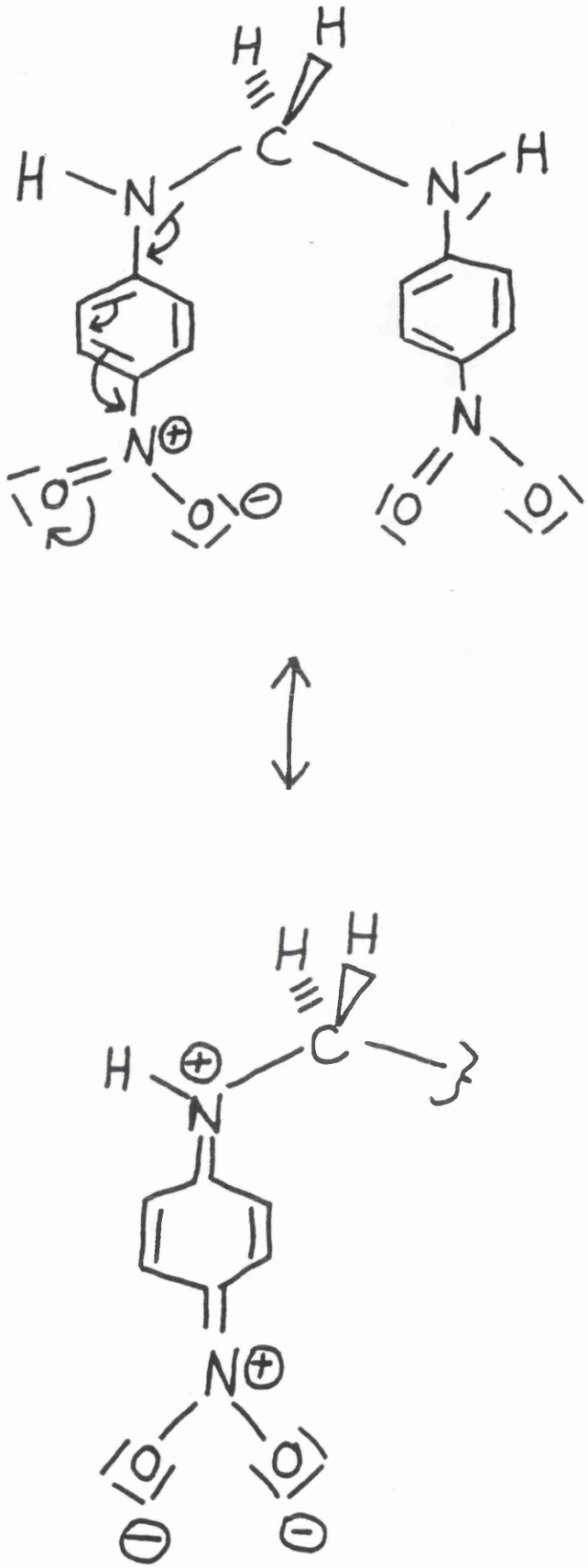
In the current work and in other formaldehyde-amine condensations carried out in this laboratory , these 1:1 condensation products have been found to be unstable and have not been isolated. This finding contrasts with the reported synthesis of N-methylene-2,6-di-isopropylaniline (4) (Verardo , Cauci & Giumanini , 1985), further condensation of which was stereochemically hindered by the presence of the bulky isopropyl substituents on the ortho positions.

The imines (iii) undergo a spontaneous nucleophilic addition reaction in basic conditions (Step 2 : Scheme 1) of a second arylamine molecule to give the 2:1 condensation products, the diaminomethanes (iv). A proposed mechanism for this step is set out of in Scheme 3.



Scheme 3

The 2:1 adducts (iv) have not been reported but we have proved that the polycondensation proceeds via such compounds by having isolated three 2:1 adducts in crystalline form. One other 2:1 adduct (iv) had been previously isolated in this laboratory and it was considered essential to verify this finding in the current work. In examining the structural features which could have led to the formation of the stable 2:1 adducts we note that each amine employed bears an electron withdrawing substituent on the ortho or para position of the phenyl ring. The resulting electron delocalisation as exemplified in Scheme 4 considerably reduces the nucleophilicity of the nitrogen lone pair.



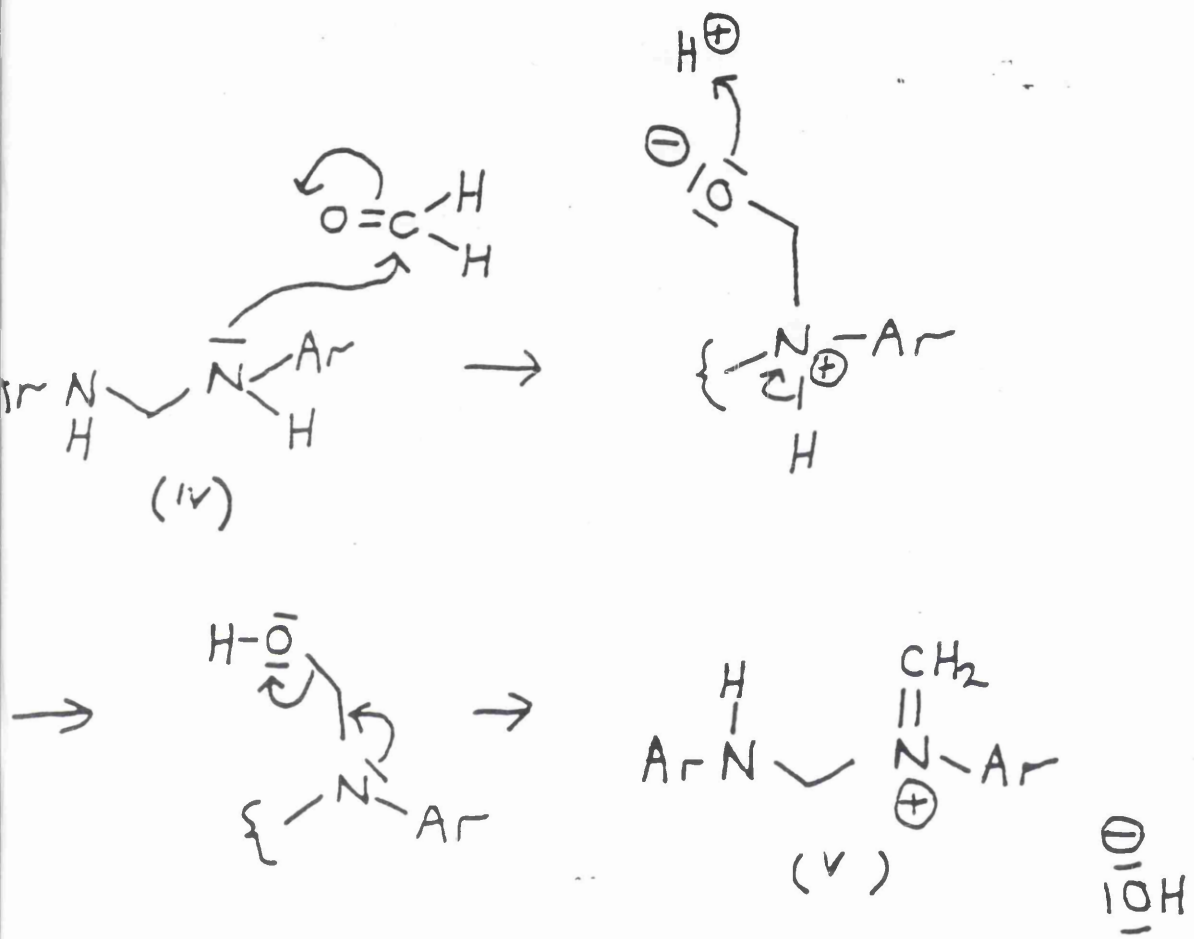
Scheme 4

The reduced nucleophilicity of the nitrogen atom of adducts considerably reduces the rate of potential reaction with a second molecule of formaldehyde. The high polarity leads to precipitation from reaction solution as a result of lowering of solubility and the creation of strong lattice forces. Both effects thus disfavour further condensation. These effects will vary with structure and it is to be expected that not all arylamines with electron withdrawing substituents on ortho or para positions will automatically terminate the poly-condensation at the 2:1 adduct stage. In fact, the reaction between formaldehyde and 4-aminobenzonitrile does not give a 2:1 adduct but leads to a higher poly-condensation product. The possibility that the further condensation of the 2:1 adduct was being prevented by steric hindrance of a substituent ortho to the aromatic amino group was considered. The reaction of 2-anisidine with formaldehyde was undertaken and compared with that of 4-anisidine. Both of these reactions lead to a higher poly-condensation product than the 2:1 adduct thus indicating that steric hindrance is not the major contributory factor to the formation of the 2:1 adducts.

In most arylamine-formaldehyde condensations the 2:1 adducts (iv) react (Step3 : Scheme 1) with a second molecule of formaldehyde (nucleophilic addition - elimination) as in Scheme 5 to form the iminium salts (v), as acyclic 2:2 adducts, the isolation of which have not been reported.

The unstable 2:2 adducts (v) can react either by intramolecular condensation between the amino-nitrogen lone pair and the iminium carbon atom (addition) as in (Step 4 : Scheme 1), the proposed mechanism shown in Scheme 6 or by intermolecular reaction with a further arylamine molecule as in (Step 5 : Scheme 1), the proposed mechanism shown in Scheme 7.

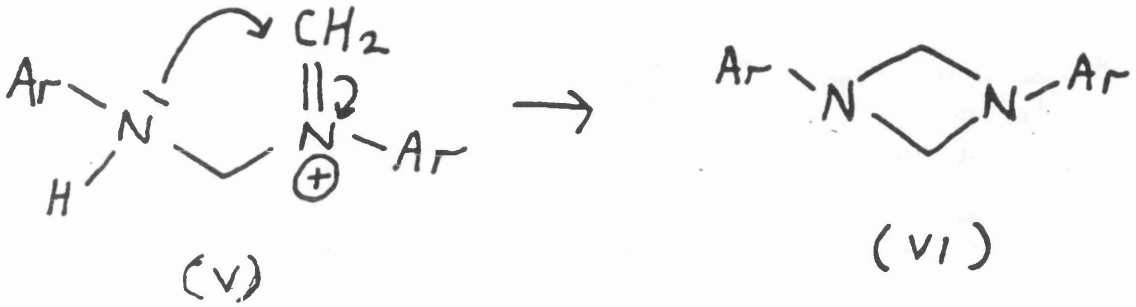
Cyclic 2:2 adducts (vi) have been reported (Verardo , Cauci & Giumanini , 1985), whereas the acyclic 3:2 (vii) adducts have never been isolated.



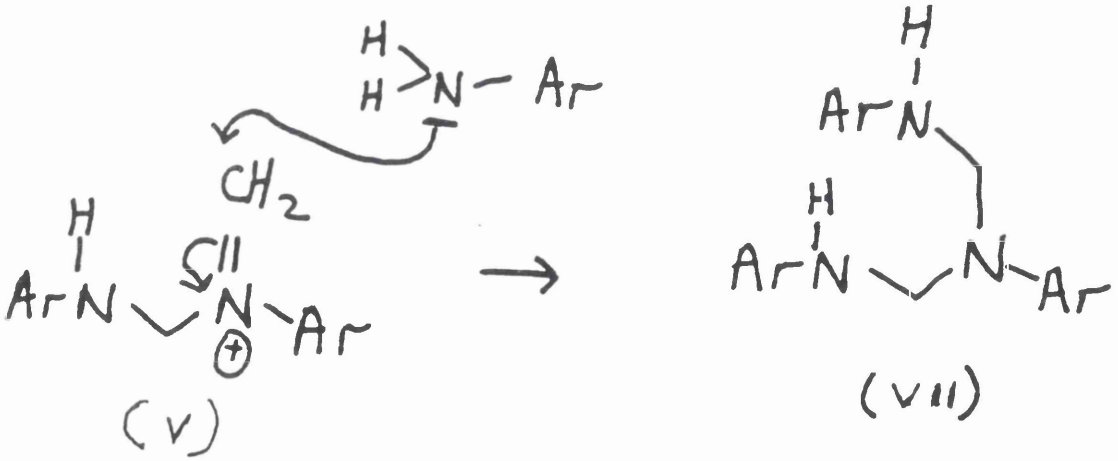
(IV)

(V)

Scheme 5



Scheme 6



Scheme 7.

In most arylamine-formaldehyde condensations the 3:2 adducts (vii) react with a further molecule of formaldehyde to form the iminium salts (viii), the isolation of which has not been reported. The iminium salt (viii) can react either by intramolecular condensation between the amino-nitrogen lone pair and the iminium carbon atom to form the stable cyclic 3:3 adducts (ix) which have been isolated in this project and also previously in this laboratory (Bouchemma, McCabe & Sim, 1988, 1989, 1990.) or by intermolecular reaction with a further arylamine molecule to form the 4:3 unstable adduct (x) which has not been isolated. This 4:3 adduct can in turn react with a further molecule of formaldehyde (Scheme 1) to form an unstable salt (xi)(4:4 adduct) which can cyclise as above to form (Scheme 1) the stable 4:4 adducts (xii) the isolation of which has been reported (Cady Larsen & Cromer, 1963; Giumanini, Gei, Randaccio & Zangrando, 1987; Choi, Abel, Dickens & Stewart, 1973).

In principle, the stepwise addition of arylamine and formaldehyde can continue from the acyclic 4:4 adducts (xi) but the higher poly-condensation products have not been characterised. It is noteworthy that the arylamine- formaldehyde condensations frequently yield intractable polymer accompanying isolable products.

X-ray investigations of 1,3,5-triaryl derivatives of 1,3,5-triazacyclohexane have consistently found the expected chair conformation with pyramidal arrangement of bonds at N atoms. The formation of the inclusion compound between 1,3,5- Tri-(p-nitrophenyl) -1,3,5-triazazcyclohexane and pyridine (**18**) has made it possible to isolate and examine the alternative twist-boat conformation.The conformation departs a little from the ideal twist-boat form presumably in response to crystal packing requirements. The incorporation of pyridine may also cause the molecule to adopt a conformation that differs from the minimum-energy conformation because of the host-guest interactions.

The formation of the inclusion compound between 1,3,5-tri-(p-nitrophenyl)-1,3,5-triazazcyclohexane and pyridine is the first reported instance of inclusion in the 1,3,5-triazacyclohexane class of compound. Since the method of synthesis of 1,3,5-triazacyclohexanes offers a wide variability of substituents , this could represent an appropriate series of compounds for future study as potential inclusion hosts. 1,3,5-triazacyclohexanes may be used in future to form inclusion compounds by crystallisation from solvents of differing polarity and shape.The selective trapping of guest molecules by inclusion lattices offers a wide variety of uses e.g. in separation, purification and controlled release. The formation of these new inclusion compounds will help the general understanding of host symmetry and inclusion behaviour. For chiral hosts, it could be possible to generate chiral cages which will offer the posssibility of enantiomeric selection from racemic guests.

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Appendix A

Geometry Tables

Table 6

Fractional coordinates for the inclusion compound between 1,3,5-Tri-(p-nitrophenyl)-1,3,5-triazazcyclohexane and pyridine (22)

	x	y	z
C(B)	0.7298(3)	0.6327(3)	-0.2066(1)
C(C)	0.8632(4)	0.6530(5)	-0.2085(1)
C(D)	0.9488(4)	0.5566(5)	-0.2059(1)
C(E)	0.8995(4)	0.4361(5)	-0.1998(1)
C(F)	0.7554(3)	0.4250(4)	-0.1965(1)
C(2)	0.5517(3)	0.2624(2)	0.0093(1)
C(4)	0.6753(2)	0.1511(2)	0.0847(1)
C(6)	0.5688(2)	0.3516(2)	0.1055(1)
C(7)	0.69209(19)	0.45359(17)	0.02885(8)
C(8)	0.7782(2)	0.5180(2)	0.0686(1)
C(9)	0.8740(2)	0.6014(2)	0.0510(1)
C(10)	0.8858(2)	0.6215(2)	-0.0072(1)
C(11)	0.8024(2)	0.5608(2)	-0.0476(1)
C(12)	0.7060(2)	0.4780(2)	-0.0302(1)
C(13)	0.43543(19)	0.09717(17)	0.06383(8)
C(14)	0.4279(2)	0.0449(2)	0.1188(1)
C(15)	0.3086(2)	-0.0072(2)	0.1356(1)
C(16)	0.1959(2)	-0.0070(2)	0.0986(1)
C(17)	0.2003(2)	0.0420(2)	0.0437(1)
C(18)	0.3194(2)	0.0931(2)	0.0268(1)
C(19)	0.70872(19)	0.24436(17)	0.18352(7)
C(20)	0.6583(2)	0.3224(2)	0.2265(1)
C(21)	0.7149(2)	0.3201(2)	0.2816(1)
C(22)	0.82145(19)	0.23869(17)	0.29580(7)
C(23)	0.8705(2)	0.1576(2)	0.2551(1)
C(24)	0.81494(19)	0.16042(18)	0.19952(8)
N(A)	0.6745(2)	0.5217(3)	-0.2004(1)
N(1)	0.59323(17)	0.37087(15)	0.04541(6)
N(3)	0.55628(16)	0.14974(14)	0.04571(6)
N(5)	0.65739(17)	0.24993(14)	0.12818(6)
N(25)	0.99102(19)	0.70584(17)	-0.02646(9)
N(26)	0.0682(2)	-0.0553(2)	0.1179(1)
N(27)	0.88302(18)	0.24072(16)	0.35350(7)
O(28)	0.99965(19)	0.72266(16)	-0.07837(8)
O(29)	1.06732(18)	0.75546(16)	0.01005(8)
O(30)	-0.03641(17)	-0.03841(17)	0.08927(7)
O(31)	0.0705(2)	-0.1111(3)	0.1634(1)
O(32)	0.84281(18)	0.31861(15)	0.38795(6)
O(33)	0.97351(18)	0.16439(16)	0.36663(6)
H(B)	0.647(5)	0.717(4)	-0.210(2)
H(C)	0.906(5)	0.745(4)	-0.208(2)
H(D)	1.033(4)	0.558(4)	-0.203(2)
H(E)	0.913(3)	0.361(2)	-0.195(1)

H(F)	0.717(3)	0.356(3)	-0.193(1)
H(2A)	0.611(2)	0.249(2)	-0.021(1)
H(2B)	0.462(2)	0.278(2)	-0.005(1)
H(4A)	0.6866(18)	0.0720(18)	0.1037(7)
H(4B)	0.755(2)	0.170(2)	0.062(1)
H(6A)	0.5861(19)	0.4308(18)	0.1282(8)
H(6B)	0.471(2)	0.330(2)	0.109(1)
H(8)	0.7758(19)	0.4992(16)	0.1082(9)
H(9)	0.932(2)	0.643(2)	0.079(1)
H(11)	0.814(2)	0.572(2)	-0.088(1)
H(12)	0.649(2)	0.437(2)	-0.059(1)
H(14)	0.501(2)	0.046(2)	0.146(1)
H(15)	0.300(2)	-0.037(2)	0.173(1)
H(17)	0.123(2)	0.035(2)	0.019(1)
H(18)	0.322(2)	0.121(2)	-0.010(1)
H(20)	0.583(2)	0.375(2)	0.216(1)
H(21)	0.6772(19)	0.3724(16)	0.3104(8)
H(23)	0.945(2)	0.098(2)	0.264(1)
H(24)	0.8514(18)	0.1065(16)	0.1721(7)

Table 7

Bond lengths for the inclusion compound between 1,3,5-Tri-(p-nitrophenyl) -1,3,5-triazazcyclohexane and pyridine (22)

C(B) - C(C)	1.334(6)	C(B) - N(A)	1.312(5)
C(B) - H(B)	1.21(5)	C(C) - C(D)	1.327(7)
C(C) - H(C)	1.07(5)	C(D) - C(E)	1.380(7)
C(D) - H(D)	0.83(5)	C(E) - C(F)	1.430(6)
C(E) - H(E)	0.82(3)	C(F) - N(A)	1.300(5)
C(F) - H(F)	0.83(3)	C(2) - N(1)	1.471(3)
C(2) - N(3)	1.465(3)	C(2) - H(2A)	0.95(3)
C(2) - H(2B)	0.95(3)	C(4) - N(3)	1.442(3)
C(4) - N(5)	1.474(3)	C(4) - H(4A)	0.95(2)
C(4) - H(4B)	0.99(2)	C(6) - N(1)	1.443(3)
C(6) - N(5)	1.469(3)	C(6) - H(6A)	1.004(19)
C(6) - H(6B)	1.00(2)	C(7) - C(8)	1.399(3)
C(7) - C(12)	1.408(3)	C(7) - N(1)	1.382(3)
C(8) - C(9)	1.373(4)	C(8) - H(8)	0.94(2)
C(9) - C(10)	1.380(4)	C(9) - H(9)	0.96(3)
C(10) - C(11)	1.374(4)	C(10) - N(25)	1.459(3)
C(11) - C(12)	1.372(4)	C(11) - H(11)	0.95(3)
C(12) - H(12)	0.96(3)	C(13) - C(14)	1.398(3)
C(13) - C(18)	1.393(3)	C(13) - N(3)	1.400(3)
C(14) - C(15)	1.375(4)	C(14) - H(14)	0.93(3)
C(15) - C(16)	1.367(4)	C(15) - H(15)	0.93(3)
C(16) - C(17)	1.379(3)	C(16) - N(26)	1.452(3)
C(17) - C(18)	1.369(3)	C(17) - H(17)	0.93(3)
C(18) - H(18)	0.903(19)	C(19) - C(20)	1.409(3)
C(19) - C(24)	1.410(3)	C(19) - N(5)	1.356(3)
C(20) - C(21)	1.368(3)	C(20) - H(20)	0.95(2)
C(21) - C(22)	1.386(3)	C(21) - H(21)	0.958(18)
C(22) - C(23)	1.386(3)	C(22) - N(27)	1.440(3)
C(23) - C(24)	1.375(3)	C(23) - H(23)	0.98(3)
C(24) - H(24)	0.943(17)	N(25) - O(28)	1.226(3)
N(25) - O(29)	1.222(3)	N(26) - O(30)	1.208(3)
N(26) - O(31)	1.211(4)	N(27) - O(32)	1.232(3)
N(27) - O(33)	1.232(3)		

Table 8

Bond angles for the inclusion compound between 1,3,5-Tri-(p-nitrophenyl) -1,3,5-triazazcyclohexane and pyridine (22)

C(C)-C(B)-N(A)	124.3(4)	C(C)-C(B)-H(B)	122.5(22)
N(A)-C(B)-H(B)	113.2(22)	C(B)-C(C)-C(D)	119.9(5)
C(B)-C(C)-H(C)	122.6(25)	C(D)-C(C)-H(C)	117.2(25)
C(C)-C(D)-C(E)	119.7(4)	C(C)-C(D)-H(D)	128.2(30)
C(E)-C(D)-H(D)	111.5(30)	C(D)-C(E)-C(F)	116.0(4)
C(D)-C(E)-H(E)	150.1(19)	C(F)-C(E)-H(E)	93.7(18)
C(E)-C(F)-N(A)	122.5(4)	C(E)-C(F)-H(F)	122.3(21)
N(A)-C(F)-H(F)	115.2(20)	N(1)-C(2)-N(3)	108.3(2)
N(1)-C(2)-H(2A)	112.2(14)	N(1)-C(2)-H(2B)	107.3(13)
N(3)-C(2)-H(2A)	107.3(13)	N(3)-C(2)-H(2B)	110.5(13)
H(2A)-C(2)-H(2B)	111.2(19)	N(3)-C(4)-N(5)	108.3(2)
N(3)-C(4)-H(4A)	110.6(11)	N(3)-C(4)-H(4B)	107.6(11)
N(5)-C(4)-H(4A)	109.2(11)	N(5)-C(4)-H(4B)	110.8(11)
H(4A)-C(4)-H(4B)	110.4(16)	N(1)-C(6)-N(5)	108.9(2)
N(1)-C(6)-H(6A)	110.9(11)	N(1)-C(6)-H(6B)	109.3(10)
N(5)-C(6)-H(6A)	110.4(11)	N(5)-C(6)-H(6B)	110.9(11)
H(6A)-C(6)-H(6B)	106.4(15)	C(8)-C(7)-C(12)	117.6(2)
C(8)-C(7)-N(1)	122.6(2)	C(12)-C(7)-N(1)	119.7(2)
C(7)-C(8)-C(9)	121.5(3)	C(7)-C(8)-H(8)	119.6(12)
C(9)-C(8)-H(8)	118.8(12)	C(8)-C(9)-C(10)	119.2(3)
C(8)-C(9)-H(9)	119.4(14)	C(10)-C(9)-H(9)	121.4(14)
C(9)-C(10)-C(11)	121.2(2)	C(9)-C(10)-N(25)	119.6(2)
C(11)-C(10)-N(25)	119.2(2)	C(10)-C(11)-C(12)	119.8(3)
C(10)-C(11)-H(11)	120.7(13)	C(12)-C(11)-H(11)	119.5(13)
C(7)-C(12)-C(11)	120.8(2)	C(7)-C(12)-H(12)	121.0(13)
C(11)-C(12)-H(12)	118.2(13)	C(14)-C(13)-C(18)	118.0(2)
C(14)-C(13)-N(3)	121.4(2)	C(18)-C(13)-N(3)	120.6(2)
C(13)-C(14)-C(15)	120.5(2)	C(13)-C(14)-H(14)	122.2(14)
C(15)-C(14)-H(14)	117.2(14)	C(14)-C(15)-C(16)	119.8(3)
C(14)-C(15)-H(15)	121.3(15)	C(16)-C(15)-H(15)	118.7(15)
C(15)-C(16)-C(17)	121.1(3)	C(15)-C(16)-N(26)	119.5(2)
C(17)-C(16)-N(26)	119.4(2)	C(16)-C(17)-C(18)	119.0(2)
C(16)-C(17)-H(17)	118.1(14)	C(18)-C(17)-H(17)	122.8(14)
C(13)-C(18)-C(17)	121.5(2)	C(13)-C(18)-H(18)	120.4(13)
C(17)-C(18)-H(18)	118.0(13)	C(20)-C(19)-C(24)	118.1(2)
C(20)-C(19)-N(5)	121.2(2)	C(24)-C(19)-N(5)	120.7(2)
C(19)-C(20)-C(21)	120.7(2)	C(19)-C(20)-H(20)	118.0(12)
C(21)-C(20)-H(20)	121.2(12)	C(20)-C(21)-C(22)	119.9(2)
C(20)-C(21)-H(21)	119.2(11)	C(22)-C(21)-H(21)	120.9(11)
C(21)-C(22)-C(23)	121.0(2)	C(21)-C(22)-N(27)	119.1(2)
C(23)-C(22)-N(27)	119.9(2)	C(22)-C(23)-C(24)	119.4(2)
C(22)-C(23)-H(23)	122.8(12)	C(24)-C(23)-H(23)	117.9(12)
C(19)-C(24)-C(23)	120.9(2)	C(19)-C(24)-H(24)	120.8(11)
C(23)-C(24)-H(24)	118.3(11)	C(B)-N(A)-C(F)	117.6(3)
C(2)-N(1)-C(6)	112.5(2)	C(2)-N(1)-C(7)	121.3(2)

C(6)-N(1)-C(7)	121.1(2)	C(2)-N(3)-C(4)	110.6(2)
C(2)-N(3)-C(13)	120.0(2)	C(4)-N(3)-C(13)	119.4(2)
C(4)-N(5)-C(6)	111.7(2)	C(4)-N(5)-C(19)	124.4(2)
C(6)-N(5)-C(19)	123.8(2)	C(10)-N(25)-O(28)	118.6(2)
C(10)-N(25)-O(29)	118.3(2)	O(28)-N(25)-O(29)	123.1(2)
C(16)-N(26)-O(30)	120.3(2)	C(16)-N(26)-O(31)	117.9(3)
O(30)-N(26)-O(31)	121.8(3)	C(22)-N(27)-O(32)	118.7(2)
C(22)-N(27)-O(33)	118.9(2)	O(32)-N(27)-O(33)	122.4(2)

Table 10

Fractional coordinates for N,N-bis-(4-methoxycarbonylphenyl) diaminomethane (34)

	x	y	z
C(1)	0.2500	-0.3047(5)	0.0000
C(2)	0.24987(19)	-0.12212(30)	0.13331(15)
C(3)	0.3572(2)	-0.1001(3)	0.1721(2)
C(4)	0.40445(19)	-0.01408(37)	0.25686(16)
C(5)	0.34794(19)	0.04780(31)	0.30616(16)
C(6)	0.2409(2)	0.0253(3)	0.2677(2)
C(7)	0.19274(19)	-0.05581(32)	0.18234(17)
C(8)	0.40276(19)	0.13706(32)	0.39736(17)
C(9)	0.3903(2)	0.2610(4)	0.5319(2)
O(1)	0.34246(14)	0.17121(26)	0.44343(11)
O(2)	0.49325(15)	0.17462(31)	0.42749(14)
N(1)	0.19917(16)	-0.20315(29)	0.04850(14)
H(C1)	0.186(2)	-0.374(4)	-0.043(2)
H(N1)	0.132(2)	-0.223(4)	0.035(2)
H(C3)	0.400(2)	-0.133(3)	0.142(2)
H(C4)	0.4785(19)	0.0003(37)	0.2779(17)
H(C6)	0.1956(18)	0.0657(34)	0.2992(16)
H(C7)	0.116(2)	-0.072(4)	0.158(2)
H(C9A)	0.338(3)	0.255(5)	0.561(2)
H(C9B)	0.456(2)	0.204(4)	0.569(2)
H(C9C)	0.421(3)	0.379(4)	0.524(2)

Table 11

Bond lengths for N,N-bis-(4-methoxycarbonylphenyl) diaminomethane (34)

C(1) - N(1)	1.450(4)	C(1) - H(C1)	1.03(4)
C(2) - C(3)	1.396(4)	C(2) - C(7)	1.395(4)
C(2) - N(1)	1.370(4)	C(3) - C(4)	1.382(4)
C(3) - H(C3)	0.92(3)	C(4) - C(5)	1.379(4)
C(4) - H(C4)	0.97(3)	C(5) - C(6)	1.392(4)
C(5) - C(8)	1.481(4)	C(6) - C(7)	1.371(4)
C(6) - H(C6)	0.99(3)	C(7) - H(C7)	0.99(3)
C(8) - O(1)	1.324(3)	C(8) - O(2)	1.205(4)
C(9) - O(1)	1.440(4)	C(9) - H(C9A)	1.00(4)
C(9) - H(C9B)	0.98(4)	C(9) - H(C9C)	1.04(4)
N(1) - H(N1)	0.90(3)		

Table 12

Bond angles for N,N-bis-(4-methoxycarbonylphenyl) diaminomethane (34)

N(1)-C(1)-N(1')	113.9(3)	N(1)-C(1)-H(C1)	97.5(17)
N(1)-C(1)-H(C1')	116.0(17)	H(C1)-C(1)-H(C1')	117.1(25)
C(3)-C(2)-C(7)	118.4(3)	C(3)-C(2)-N(1)	122.3(3)
C(7)-C(2)-N(1)	119.3(3)	C(2)-C(3)-C(4)	120.1(3)
C(2)-C(3)-H(C3)	123.6(17)	C(4)-C(3)-H(C3)	116.2(17)
C(3)-C(4)-C(5)	121.3(3)	C(3)-C(4)-H(C4)	115.4(16)
C(5)-C(4)-H(C4)	123.3(16)	C(4)-C(5)-C(6)	118.6(3)
C(4)-C(5)-C(8)	119.1(3)	C(6)-C(5)-C(8)	122.4(3)
C(5)-C(6)-C(7)	120.7(3)	C(5)-C(6)-H(C6)	123.0(14)
C(7)-C(6)-H(C6)	116.3(14)	C(2)-C(7)-C(6)	120.9(3)
C(2)-C(7)-H(C7)	120.7(15)	C(6)-C(7)-H(C7)	118.4(15)
C(5)-C(8)-O(1)	113.3(3)	C(5)-C(8)-O(2)	123.8(3)
O(1)-C(8)-O(2)	122.9(3)	O(1)-C(9)-H(C9A)	104.2(20)
O(1)-C(9)-H(C9B)	108.0(19)	O(1)-C(9)-H(C9C)	112.3(19)
H(C9A)-C(9)-H(C9B)	114.0(28)	H(C9A)-C(9)-H(C9C)	120.7(30)
H(C9B)-C(9)-H(C9C)	97.3(28)	C(8)-O(1)-C(9)	116.3(3)
C(1)-N(1)-H(N1)	118.1(18)	C(1)-N(1)-C(2)	124.2(2)
C(2)-N(1)-H(N1)	113.9(17)		

Table 13

Fractional coordinates for N,N-bis-(2-trifluorophenyl) diaminomethane (36)

	x	y	z
C(8)	0.7504(3)	0.4649(6)	0.6262(2)
C(1A)	0.65681(15)	0.79503(54)	0.62645(10)
C(2A)	0.62470(18)	0.97262(58)	0.65003(13)
C(3A)	0.57205(18)	1.14454(72)	0.62645(10)
C(4A)	0.5507(2)	1.1433(8)	0.5794(1)
C(5A)	0.5814(2)	0.9695(8)	0.5558(1)
C(6A)	0.63337(19)	0.79848(72)	0.57892(12)
C(7A)	0.6464(2)	0.9833(7)	0.7007(2)
C(1B)	0.84349(15)	0.79590(57)	0.62476(11)
C(2B)	0.8753(2)	0.9675(6)	0.6003(1)
C(3B)	0.92737(19)	1.14399(69)	0.62236(14)
C(4B)	0.9493(2)	1.1538(8)	0.6694(2)
C(5B)	0.9191(2)	0.9841(8)	0.6934(2)
C(6B)	0.86747(18)	0.81167(75)	0.67240(12)
C(7B)	0.8520(3)	0.9663(8)	0.5495(2)
N(A)	0.70928(14)	0.62601(53)	0.64920(10)
N(B)	0.79072(14)	0.62369(54)	0.60337(10)
F(1A)	0.71076(14)	1.06967(51)	0.71758(8)
F(2A)	0.64363(13)	0.74628(44)	0.71995(6)
F(3A)	0.60619(15)	1.14558(53)	0.71729(8)
F(1B)	0.78651(15)	1.05180(57)	0.53285(9)
F(2B)	0.85378(13)	0.72399(46)	0.53108(7)
F(3B)	0.89042(16)	1.12531(51)	0.53066(8)
H(81)	0.7814(16)	0.3539(59)	0.6497(11)
H(82)	0.7184(17)	0.3247(69)	0.6040(11)
H(3A)	0.5523(18)	1.2576(64)	0.6428(11)
H(4A)	0.5197(19)	1.2451(51)	0.5650(11)
H(5A)	0.564(2)	0.937(7)	0.522(1)
H(6A)	0.6578(16)	0.7164(58)	0.5627(10)
H(3B)	0.9452(16)	1.2624(61)	0.6056(10)
H(4B)	0.9855(19)	1.2705(72)	0.6864(12)
H(5B)	0.9340(18)	0.9858(72)	0.7278(13)
H(6B)	0.8475(17)	0.7071(63)	0.6898(10)
H(NA)	0.727(2)	0.667(7)	0.680(1)
H(NB)	0.7805(16)	0.6038(58)	0.5743(11)

Table 14

Bond lengths for N,N-bis-(2-trifluorophenyl) diaminomethane (36)

C(8) - N(A)	1.459(6)	C(8) - N(B)	1.439(6)
C(8) - H(81)	0.97(4)	C(8) - H(82)	1.05(4)
C(1A) - C(2A)	1.402(5)	C(1A) - C(6A)	1.394(5)
C(1A) - N(A)	1.372(4)	C(2A) - C(3A)	1.391(5)
C(2A) - C(7A)	1.484(6)	C(3A) - C(4A)	1.377(6)
C(3A) - H(3A)	0.91(4)	C(4A) - C(5A)	1.373(6)
C(4A) - H(4A)	0.82(4)	C(5A) - C(6A)	1.376(6)
C(5A) - H(5A)	1.01(5)	C(6A) - H(6A)	0.89(3)
C(7A) - F(1A)	1.318(5)	C(7A) - F(2A)	1.323(5)
C(7A) - F(3A)	1.335(5)	C(1B) - C(2B)	1.398(5)
C(1B) - C(6B)	1.400(5)	C(1B) - N(B)	1.374(4)
C(2B) - C(3B)	1.385(6)	C(2B) - C(7B)	1.488(7)
C(3B) - C(4B)	1.378(7)	C(3B) - H(3B)	0.92(4)
C(4B) - C(5B)	1.365(6)	C(4B) - H(4B)	0.96(4)
C(5B) - C(6B)	1.357(6)	C(5B) - H(5B)	1.01(4)
C(6B) - H(6B)	0.91(4)	C(7B) - F(1B)	1.336(6)
C(7B) - F(2B)	1.331(5)	C(7B) - F(3B)	1.337(6)
N(A) - H(NA)	0.94(4)	N(B) - H(NB)	0.86(4)

Table 15

Bond angles for N,N-bis-(2-trifluorophenyl) diaminomethane (36)

N(A)-C(8)-N(B)	113.6(3)	N(A)-C(8)-H(81)	106.6
N(A)-C(8)-H(82)	110.3	N(B)-C(8)-H(81)	109.6
N(B)-C(8)-H(82)	111.9	H(81)-C(8)-H(82)	104.3
C(2A)-C(1A)-C(6A)	117.1(3)	C(2A)-C(1A)-N(A)	121.4(3)
C(6A)-C(1A)-N(A)	121.5(3)	C(1A)-C(2A)-C(3A)	120.6(4)
C(1A)-C(2A)-C(7A)	120.9(3)	C(3A)-C(2A)-C(7A)	118.5(4)
C(2A)-C(3A)-C(4A)	120.5(4)	C(2A)-C(3A)-H(3A)	118.3
C(4A)-C(3A)-H(3A)	121.2	C(3A)-C(4A)-C(5A)	119.6(4)
C(3A)-C(4A)-H(4A)	121.2	C(5A)-C(4A)-H(4A)	119.1
C(4A)-C(5A)-C(6A)	120.2(5)	C(4A)-C(5A)-H(5A)	124.5
C(6A)-C(5A)-H(5A)	114.8	C(1A)-C(6A)-C(5A)	121.9(4)
C(1A)-C(6A)-H(6A)	119.8	C(5A)-C(6A)-H(6A)	117.0
C(2A)-C(7A)-F(1A)	112.9(4)	C(2A)-C(7A)-F(2A)	113.2(3)
C(2A)-C(7A)-F(3A)	112.6(4)	F(1A)-C(7A)-F(2A)	105.8(4)
F(1A)-C(7A)-F(3A)	106.4(4)	F(2A)-C(7A)-F(3A)	105.2(4)
C(2B)-C(1B)-C(6B)	116.5(3)	C(2B)-C(1B)-N(B)	122.0(4)
C(6B)-C(1B)-N(B)	121.6(3)	C(1B)-C(2B)-C(3B)	121.2(4)
C(1B)-C(2B)-C(7B)	119.8(4)	C(3B)-C(2B)-C(7B)	119.0(4)
C(2B)-C(3B)-C(4B)	120.5(4)	C(2B)-C(3B)-H(3B)	119.5
C(4B)-C(3B)-H(3B)	119.9	C(3B)-C(4B)-C(5B)	118.5(4)
C(3B)-C(4B)-H(4B)	123.9	C(5B)-C(4B)-H(4B)	117.6
C(4B)-C(5B)-C(6B)	121.9(4)	C(4B)-C(5B)-H(5B)	120.5
C(6B)-C(5B)-H(5B)	117.6	C(1B)-C(6B)-C(5B)	121.4(4)
C(1B)-C(6B)-H(6B)	119.5	C(5B)-C(6B)-H(6B)	119.0
C(2B)-C(7B)-F(1B)	112.5(4)	C(2B)-C(7B)-F(2B)	113.8(4)
C(2B)-C(7B)-F(3B)	113.1(4)	F(1B)-C(7B)-F(2B)	105.4(4)
F(1B)-C(7B)-F(3B)	105.7(4)	F(2B)-C(7B)-F(3B)	105.4(4)
C(8)-N(A)-C(1A)	123.1(4)	C(8)-N(A)-H(NA)	119.9
C(1A)-N(A)-H(NA)	113.5	C(8)-N(B)-C(1B)	124.9(4)
C(8)-N(B)-H(NB)	115.6	C(1B)-N(B)-H(NB)	119.6

Table 17

Fractional coordinates for 1,3,5-tri-(4-cyanophenyl)-1,3,5-triazacyclohexa ne (41)

	x	y	z
C(1A)	0.3252(11)	0.4630(15)	0.0577(35)
C(2A)	0.3758(13)	0.5553(15)	0.1315(38)
C(3A)	0.4224(13)	0.4618(17)	0.0753(39)
C(11A)	0.3748(12)	0.3615(16)	0.0009(34)
C(12A)	0.4163(14)	0.3265(17)	-0.0622(38)
C(13A)	0.4146(11)	0.2553(16)	-0.0681(35)
C(14A)	0.3814(15)	0.2218(14)	-0.0143(40)
C(15A)	0.3364(16)	0.2543(23)	0.0394(49)
C(16A)	0.3302(14)	0.3225(19)	0.0629(44)
C(17A)	0.3783(16)	0.1466(17)	-0.0159(39)
C(21A)	0.3148(12)	0.5620(16)	-0.1185(33)
C(22A)	0.3099(13)	0.5165(16)	-0.2664(36)
C(23A)	0.3009(12)	0.5453(17)	-0.4344(36)
C(24A)	0.2915(12)	0.6117(20)	-0.4458(33)
C(25A)	0.2935(13)	0.6589(20)	-0.2722(40)
C(26A)	0.3080(12)	0.6270(16)	-0.1318(35)
C(27A)	0.2907(14)	0.6449(17)	-0.6119(34)
C(31A)	0.4358(12)	0.5547(16)	-0.0749(38)
C(32A)	0.4439(15)	0.5153(17)	-0.2418(39)
C(33A)	0.4507(13)	0.5516(17)	-0.4015(34)
C(34A)	0.4582(12)	0.6155(16)	-0.4046(32)
C(35A)	0.4580(16)	0.6537(17)	-0.2471(42)
C(36A)	0.4457(14)	0.6268(17)	-0.0876(40)
C(37A)	0.4656(15)	0.6473(20)	-0.5488(40)
C(1B)	0.1752(14)	0.9559(16)	0.4396(46)
C(2B)	0.1281(14)	1.0657(19)	0.3701(38)
C(3B)	0.0795(13)	0.9557(17)	0.4144(43)
C(11B)	0.1281(15)	0.8567(16)	0.5061(41)
C(12B)	0.1671(12)	0.8188(18)	0.4642(40)
C(13B)	0.1686(12)	0.7535(16)	0.4617(33)
C(14B)	0.1280(15)	0.7221(16)	0.5150(38)
C(15B)	0.0746(16)	0.7628(21)	0.5816(43)
C(16B)	0.0815(14)	0.8280(18)	0.5747(45)
C(17B)	0.1245(19)	0.6551(18)	0.5183(45)
C(21B)	0.1867(13)	1.0536(17)	0.6413(41)
C(22B)	0.1899(12)	1.0230(15)	0.7844(43)
C(23B)	0.2003(13)	1.0530(18)	0.9288(43)
C(24B)	0.2063(14)	1.1201(17)	0.9418(40)
C(25B)	0.2009(15)	1.1536(16)	0.8223(38)
C(26B)	0.1971(14)	1.1258(18)	0.6458(44)
C(27B)	0.2187(17)	1.1520(22)	1.0938(57)
C(31B)	0.0643(12)	1.0593(16)	0.6208(39)
C(32B)	0.0619(12)	1.0216(16)	0.7346(38)
C(33B)	0.0454(13)	1.0463(18)	0.8788(45)
C(34B)	0.0375(16)	1.1154(19)	0.8908(49)

C(35B)	0.0462(14)	1.1566(18)	0.7557(41)
C(36B)	0.0556(13)	1.1261(17)	0.6184(40)
C(37B)	0.0293(16)	1.1494(18)	1.0732(44)
N(1A)	0.3745(9)	0.4307(11)	-0.0009(28)
N(2A)	0.3248(11)	0.5299(13)	0.0362(31)
N(3A)	0.4217(10)	0.5334(13)	0.0604(28)
N(11A)	0.3778(16)	0.0855(16)	-0.0182(41)
N(22A)	0.2815(12)	0.6753(17)	-0.7271(31)
N(33A)	0.4805(16)	0.6666(19)	-0.6824(38)
N(1B)	0.1286(11)	0.9253(14)	0.5010(35)
N(2B)	0.1722(10)	1.0320(13)	0.4563(32)
N(3B)	0.0780(11)	1.0271(14)	0.4393(33)
N(11B)	0.1190(16)	0.6008(15)	0.5298(38)
N(22B)	0.223(2)	1.171(2)	1.254(5)
N(33B)	0.0274(13)	1.1774(17)	1.1907(37)
H(1A)	0.31224	0.43639	0.22995
H(2A)	0.27933	0.43173	-0.04594
H(3A)	0.34508	0.56846	0.35417
H(4A)	0.39768	0.63180	-0.01778
H(5A)	0.46138	0.41759	0.06763
H(6A)	0.43117	0.50822	0.05307
H(7A)	0.46460	0.35520	0.16113
H(8A)	0.43650	0.24923	0.06062
H(9A)	0.42933	0.17790	0.08071
H(10A)	0.31130	0.21713	0.19487
H(11A)	0.29948	0.46425	-0.31851
H(12A)	0.30739	0.53783	-0.57874
H(13A)	0.34775	0.72203	-0.03764
H(14A)	0.28992	0.68775	-0.22229
H(15A)	0.44212	0.47154	-0.28003
H(16A)	0.43622	0.53314	-0.46720
H(17A)	0.42809	0.64659	-0.51963
H(18A)	0.45576	0.67343	-0.27047
H(1B)	0.19894	0.93522	0.49706
H(2B)	0.21130	1.04768	0.40649
H(3B)	0.08287	1.04411	0.21007
H(4B)	0.16623	1.12762	0.36301
H(5B)	0.05256	0.94756	0.47553
H(6B)	0.08666	0.95502	0.26082
H(7B)	0.20201	0.84772	0.48432
H(8B)	0.18999	0.72636	0.48945
H(10B)	0.05762	0.73404	0.65286
H(11B)	0.17517	0.97467	0.72147
H(12B)	0.21986	1.03230	0.94879
H(13B)	0.18732	1.12255	0.88896
H(14B)	0.19987	1.22277	0.93679
H(15B)	0.08769	0.96525	0.75519
H(16B)	0.05264	1.04669	1.19788
H(17B)	0.03905	1.14812	0.97615
H(18B)	0.05260	1.21690	0.73291

Table 18

Bond lengths for 1,3,5-tri-(4-cyanophenyl)-1,3,5-triazacyclohexane (41)

C(1A) - N(1A)	1.52(4)	C(1A) - N(2A)	1.37(5)
C(2A) - N(2A)	1.55(5)	C(2A) - N(3A)	1.41(5)
C(3A) - N(1A)	1.47(5)	C(3A) - N(3A)	1.46(5)
C(3A) - H(6A)	0.99(4)	C(11A)- C(12A)	1.40(5)
C(11A)- C(16A)	1.50(5)	C(11A)- N(1A)	1.40(4)
C(12A)- C(13A)	1.44(5)	C(13A)- C(14A)	1.19(5)
C(13A)- H(8A)	1.13(3)	C(14A)- C(15A)	1.41(6)
C(14A)- C(17A)	1.53(5)	C(15A)- C(16A)	1.40(6)
C(17A)- N(11A)	1.24(5)	C(21A)- C(22A)	1.48(5)
C(21A)- C(26A)	1.33(5)	C(21A)- N(2A)	1.39(4)
C(22A)- C(23A)	1.45(5)	C(22A)- H(11A)	1.16(4)
C(23A)- C(24A)	1.37(6)	C(23A)- H(12A)	1.17(3)
C(24A)- C(25A)	1.67(5)	C(24A)- C(27A)	1.47(5)
C(25A)- C(26A)	1.31(5)	C(25A)- H(14A)	0.71(4)
C(27A)- N(22A)	1.11(5)	C(31A)- C(32A)	1.56(5)
C(31A)- C(36A)	1.49(5)	C(31A)- N(3A)	1.23(4)
C(32A)- C(33A)	1.48(5)	C(32A)- H(15A)	0.94(4)
C(33A)- C(34A)	1.31(5)	C(33A)- H(16A)	0.72(4)
C(34A)- C(35A)	1.46(5)	C(34A)- C(37A)	1.33(5)
C(35A)- C(36A)	1.42(5)	C(35A)- H(18A)	0.44(4)
C(37A)- N(33A)	1.21(5)	C(37A)- H(17A)	1.00(4)
C(1B) - N(1B)	1.46(5)	C(1B) - N(2B)	1.55(5)
C(1B) - H(1B)	0.84(4)	C(2B) - N(2B)	1.45(5)
C(2B) - N(3B)	1.63(5)	C(3B) - N(1B)	1.52(5)
C(3B) - N(3B)	1.46(5)	C(3B) - H(5B)	0.88(4)
C(3B) - H(6B)	1.24(4)	C(11B)- C(12B)	1.32(5)
C(11B)- C(16B)	1.46(6)	C(11B)- N(1B)	1.39(5)
C(12B)- C(13B)	1.32(5)	C(12B)- H(7B)	1.07(4)
C(13B)- C(14B)	1.31(5)	C(13B)- H(8B)	0.80(4)
C(14B)- C(17B)	1.36(5)	C(15B)- C(16B)	1.33(6)
C(15B)- H(10B)	0.94(4)	C(17B)- N(11B)	1.11(5)
C(21B)- C(22B)	1.28(5)	C(21B)- C(26B)	1.49(5)
C(21B)- N(2B)	1.54(5)	C(22B)- C(23B)	1.30(5)
C(22B)- H(11B)	1.15(4)	C(23B)- C(24B)	1.37(5)
C(23B)- H(12B)	0.66(4)	C(24B)- C(25B)	1.16(5)
C(24B)- C(27B)	1.38(6)	C(24B)- H(13B)	0.62(4)
C(25B)- C(26B)	1.50(5)	C(25B)- H(13B)	0.90(4)
C(27B)- N(22B)	1.32(6)	C(31B)- C(32B)	1.18(5)
C(31B)- C(36B)	1.37(5)	C(31B)- N(3B)	1.63(5)
C(32B)- C(33B)	1.34(5)	C(33B)- C(34B)	1.42(6)
C(34B)- C(35B)	1.38(6)	C(34B)- C(37B)	1.62(6)
C(34B)- H(17B)	0.94(4)	C(35B)- C(36B)	1.28(5)
C(35B)- H(18B)	1.25(4)	C(37B)- N(33B)	1.09(5)
C(37B)- H(17B)	0.82(4)	N(3A) - H(6A)	0.57(3)
N(2B) - H(2B)	1.14(3)	H(3B) - H(16B)	0.775

Table 19

Bond angles for 1,3,5-tri-(4-cyanophenyl)-1,3,5-triazacyclohexane (41)

N(1A)-C(1A)-N(2A)	112.9(24)	N(2A)-C(2A)-N(3A)	113.6(24)
N(1A)-C(3A)-N(3A)	112.8(26)	N(1A)-C(3A)-H(6A)	122.0(30)
N(3A)-C(3A)-H(6A)	15.4(13)	C(12A)-C(11A)-C(16A)	117.6(30)
C(12A)-C(11A)-N(1A)	120.5(28)	C(16A)-C(11A)-N(1A)	121.8(27)
C(11A)-C(12A)-C(13A)	119.8(30)	C(12A)-C(13A)-C(14A)	125.4(31)
C(12A)-C(13A)-H(8A)	93.9(24)	C(14A)-C(13A)-H(8A)	86.6(25)
C(13A)-C(14A)-C(15A)	117.3(33)	C(13A)-C(14A)-C(17A)	127.2(34)
C(15A)-C(14A)-C(17A)	115.0(33)	C(14A)-C(15A)-C(16A)	126.8(37)
C(11A)-C(16A)-C(15A)	112.4(32)	C(14A)-C(17A)-N(11A)	177.4(41)
C(22A)-C(21A)-C(26A)	123.2(26)	C(22A)-C(21A)-N(2A)	113.6(28)
C(26A)-C(21A)-N(2A)	123.1(27)	C(21A)-C(22A)-C(23A)	117.9(29)
C(21A)-C(22A)-H(11A)	148.1(28)	C(23A)-C(22A)-H(11A)	91.5(23)
C(22A)-C(23A)-C(24A)	118.1(28)	C(22A)-C(23A)-H(12A)	144.2(32)
C(24A)-C(23A)-H(12A)	95.7(25)	C(23A)-C(24A)-C(25A)	121.0(26)
C(23A)-C(24A)-C(27A)	120.0(28)	C(25A)-C(24A)-C(27A)	117.8(32)
C(24A)-C(25A)-C(26A)	113.6(32)	C(24A)-C(25A)-H(14A)	157.5(41)
C(26A)-C(25A)-H(14A)	88.7(32)	C(21A)-C(26A)-C(25A)	125.5(30)
C(24A)-C(27A)-N(22A)	166.4(37)	C(32A)-C(31A)-C(36A)	114.3(26)
C(32A)-C(31A)-N(3A)	128.0(30)	C(36A)-C(31A)-N(3A)	117.7(28)
C(31A)-C(32A)-C(33A)	119.5(28)	C(31A)-C(32A)-H(15A)	138.4(32)
C(33A)-C(32A)-H(15A)	101.7(28)	C(32A)-C(33A)-C(34A)	122.3(27)
C(32A)-C(33A)-H(16A)	105.6(35)	C(34A)-C(33A)-H(16A)	124.7(36)
C(33A)-C(34A)-C(35A)	119.8(27)	C(33A)-C(34A)-C(37A)	121.6(29)
C(35A)-C(34A)-C(37A)	118.6(32)	C(34A)-C(35A)-C(36A)	124.1(30)
C(34A)-C(35A)-H(18A)	97.6(49)	C(36A)-C(35A)-H(18A)	132.9(58)
C(31A)-C(36A)-C(35A)	118.9(29)	C(34A)-C(37A)-N(33A)	166.3(42)
C(34A)-C(37A)-H(17A)	66.7(24)	N(33A)-C(37A)-H(17A)	124.7(38)
N(1B)-C(1B)-N(2B)	110.3(27)	N(1B)-C(1B)-H(1B)	100.7(32)
N(2B)-C(1B)-H(1B)	119.1(34)	N(2B)-C(2B)-N(3B)	102.9(26)
N(1B)-C(3B)-N(3B)	111.7(27)	N(1B)-C(3B)-H(5B)	109.4(31)
N(1B)-C(3B)-H(6B)	105.3(25)	N(3B)-C(3B)-H(5B)	94.7(29)
N(3B)-C(3B)-H(6B)	98.6(25)	H(5B)-C(3B)-H(6B)	134.8(35)
C(12B)-C(11B)-C(16B)	120.8(31)	C(12B)-C(11B)-N(1B)	124.4(33)
C(16B)-C(11B)-N(1B)	114.7(31)	C(11B)-C(12B)-C(13B)	127.4(33)
C(11B)-C(12B)-H(7B)	106.5(32)	C(13B)-C(12B)-H(7B)	121.7(31)
C(12B)-C(13B)-C(14B)	117.2(31)	C(12B)-C(13B)-H(8B)	134.9(36)
C(14B)-C(13B)-H(8B)	97.0(32)	C(13B)-C(14B)-C(17B)	123.0(37)
C(16B)-C(15B)-H(10B)	135.1(41)	C(11B)-C(16B)-C(15B)	121.5(34)
C(14B)-C(17B)-N(11B)	174.8(47)	C(22B)-C(21B)-C(26B)	117.0(31)
C(22B)-C(21B)-N(2B)	133.6(31)	C(26B)-C(21B)-N(2B)	109.4(27)
C(21B)-C(22B)-C(23B)	122.6(32)	C(21B)-C(22B)-H(11B)	91.9(28)
C(23B)-C(22B)-H(11B)	144.8(33)	C(22B)-C(23B)-C(24B)	122.9(33)
C(22B)-C(23B)-H(12B)	91.1(37)	C(24B)-C(23B)-H(12B)	122.1(42)
C(23B)-C(24B)-C(25B)	120.7(34)	C(23B)-C(24B)-C(27B)	123.1(34)
C(23B)-C(24B)-H(13B)	87.1(37)	C(25B)-C(24B)-C(27B)	116.1(36)
C(25B)-C(24B)-H(13B)	50.5(30)	C(27B)-C(24B)-H(13B)	132.1(46)

C(24B)-C(25B)-C(26B)	122.1(33)	C(24B)-C(25B)-H(13B)	32.0(21)
C(26B)-C(25B)-H(13B)	106.0(31)	C(21B)-C(26B)-C(25B)	113.0(29)
C(24B)-C(27B)-N(22B)	165.6(46)	C(32B)-C(31B)-C(36B)	129.1(33)
C(32B)-C(31B)-N(3B)	115.6(30)	C(36B)-C(31B)-N(3B)	115.3(27)
C(31B)-C(32B)-C(33B)	116.1(33)	C(32B)-C(33B)-C(34B)	118.7(33)
C(33B)-C(34B)-C(35B)	120.9(35)	C(33B)-C(34B)-C(37B)	120.4(32)
C(33B)-C(34B)-H(17B)	137.9(40)	C(35B)-C(34B)-C(37B)	117.6(33)
C(35B)-C(34B)-H(17B)	97.1(34)	C(37B)-C(34B)-H(17B)	21.6(18)
C(34B)-C(35B)-C(36B)	114.1(35)	C(34B)-C(35B)-H(18B)	137.0(32)
C(36B)-C(35B)-H(18B)	108.4(29)	C(31B)-C(36B)-C(35B)	120.2(32)
C(34B)-C(37B)-N(33B)	172.3(41)	C(34B)-C(37B)-H(17B)	25.1(21)
N(33B)-C(37B)-H(17B)	147.4(48)	C(1A)-N(1A)-C(3A)	112.2(22)
C(1A)-N(1A)-C(11A)	115.6(23)	C(3A)-N(1A)-C(11A)	114.8(24)
C(1A)-N(2A)-C(2A)	105.7(24)	C(1A)-N(2A)-C(21A)	124.9(26)
C(2A)-N(2A)-C(21A)	111.7(25)	C(2A)-N(3A)-C(3A)	106.8(24)
C(2A)-N(3A)-C(31A)	122.5(27)	C(2A)-N(3A)-H(6A)	134.1(35)
C(3A)-N(3A)-C(31A)	114.7(26)	C(3A)-N(3A)-H(6A)	27.4(22)
C(31A)-N(3A)-H(6A)	94.2(30)	C(1B)-N(1B)-C(3B)	110.5(26)
C(1B)-N(1B)-C(11B)	116.4(28)	C(3B)-N(1B)-C(11B)	114.1(28)
C(1B)-N(2B)-C(2B)	118.1(26)	C(1B)-N(2B)-C(21B)	110.6(24)
C(1B)-N(2B)-H(2B)	101.3(22)	C(2B)-N(2B)-C(21B)	116.1(25)
C(2B)-N(2B)-H(2B)	112.4(24)	C(21B)-N(2B)-H(2B)	94.9(21)
C(2B)-N(3B)-C(3B)	113.7(26)	C(2B)-N(3B)-C(31B)	108.8(23)
C(3B)-N(3B)-C(31B)	121.5(25)	C(3A)-H(6A)-N(3A)	137.2(32)
C(24B)-H(13B)-C(25B)	97.6(39)	C(34B)-H(17B)-C(37B)	133.3(35)

Table 20

Fractional coordinates for 1,3,5-tri-(2-methoxyphenyl)-1,3,5-triazacyclohex ane (43)

	x	y	z
N(1)	0.25853(13)	0.08060(13)	0.68684(6)
N(3)	0.33540(13)	0.18870(13)	0.84249(7)
N(5)	0.48220(13)	0.37244(13)	0.73449(7)
C(2)	0.19546(17)	0.07206(18)	0.77244(8)
C(4)	0.40923(18)	0.36012(17)	0.81789(9)
C(6)	0.34826(17)	0.25336(16)	0.66506(9)
C(7)	0.32254(15)	-0.03352(15)	0.65823(8)
C(8)	0.29521(16)	-0.09136(16)	0.56773(8)
C(9)	0.3415(2)	-0.2134(2)	0.5376(1)
C(10)	0.4134(2)	-0.2798(2)	0.5964(1)
C(11)	0.4415(2)	-0.2239(2)	0.6844(1)
C(12)	0.39686(18)	-0.10042(18)	0.71533(10)
C(13)	0.28214(17)	0.17356(19)	0.92917(9)
C(14)	0.2660(2)	0.0337(2)	0.9695(1)
C(15)	0.2264(3)	0.0207(3)	1.0558(1)
C(16)	0.1994(3)	0.1428(4)	1.1019(1)
C(17)	0.2105(2)	0.2777(3)	1.0638(1)
C(18)	0.2527(2)	0.2942(3)	0.9771(1)
C(19)	0.65731(15)	0.39246(15)	0.73592(8)
C(20)	0.76807(16	0.49279(15)	0.67727(8)
C(21)	0.94431(17)	0.52968(17)	0.68244(10)
C(22)	1.01164(18)	0.46722(19)	0.74507(11)
C(23)	0.90477(19	0.36692(20)	0.80178(10)
C(24)	0.72819(18)	0.32961(18)	0.79704(9)
C(25)	0.1662(2)	-0.0947(2)	0.4252(1)
C(26)	0.2786(3)	-0.2289(3)	0.9538(1)
C(27)	0.8090(2)	0.6687(2)	0.5644(1)
O(1)	0.21717(13)	-0.02354(12)	0.51519(6)
O(2)	0.29630(18)	-0.08078(16)	0.91908(7)
O(3)	0.69286(12)	0.55057(13)	0.61719(7)
H(2A)	0.102(2)	0.108(2)	0.769(1)
H(2B)	0.1461(18)	-0.0415(18)	0.7867(9)
H(4A)	0.4973(18)	0.43860(17)	0.8657(9)
H(4B)	0.319(2)	0.401(2)	0.810(1)
H(6A)	0.4037(17)	0.2539(16)	0.6105(8)
H(6B)	0.258(2)	0.292(2)	0.656(1)
H(9)	0.321(2)	-0.254(2)	0.477(1)
H(10)	0.440(20	-0.365(2)	0.576(1)
H(11)	0.489(2)	-0.268(2)	0.726(1)
H(12)	0.414(2)	-0.060(2)	0.775(1)
H(15)	0.216(3)	-0.075(3)	1.078(1)
H(16)	0.174(3)	0.138(3)	1.162(2)
H(17)	0.189(3)	0.362(3)	1.096(1)
H(18)	0.270(2)	0.395(2)	0.953(1)

H(21)	1.020(2)	0.599(2)	0.645(1)
H(22)	1.136(2)	0.499(2)	0.749(1)
H(23)	0.950(2)	0.320(20	0.845(1)
H(24)	0.658(2)	0.263(2)	0.838(1)
H(25A)	0.100(3)	-0.042(3)	0.401(1)
H(25B)	0.092(2)	-0.217(3)	0.419(1)
H(25C)	0.266(3)	-0.068(3)	0.395(1)
H(26A)	0.160(4)	-0.293(3)	0.968(2)
H(26B)	0.355(3)	-0.194(3)	1.007(2)
H(26C)	0.303(4)	-0.293(3)	0.904(2)
H(27A)	0.738(3)	0.700(2)	0.531(1)
H(27B)	0.857(3)	0.608(3)	0.523(1)
H(27C)	0.905(3)	0.764(30	0.601(1)

Table 21

Bond lengths for 1,3,5-tri-(2-methoxyphenyl)-1,3,5-triazacyclohexane (43)

N(1) - C(2)	1.445(2)	N(1) - C(6)	1.459(2)
N(1) - C(7)	1.422(2)	N(3) - C(2)	1.481(2)
N(3) - C(4)	1.464(2)	N(3) - C(13)	1.429(2)
N(5) - C(4)	1.448(2)	N(5) - C(6)	1.460(2)
N(5) - C(19)	1.427(2)	C(2) - H(2A)	0.996(16)
C(2) - H(2B)	0.959(15)	C(4) - H(4A)	0.981(14)
C(4) - H(4B)	1.005(16)	C(6) - H(6A)	0.987(14)
C(6) - H(6B)	0.993(15)	C(7) - C(8)	1.408(2)
C(7) - C(12)	1.386(2)	C(8) - C(9)	1.384(3)
C(8) - O(1)	1.368(2)	C(9) - C(10)	1.386(3)
C(9) - H(9)	0.947(17)	C(10) - C(11)	1.368(3)
C(10) - H(10)	0.929(19)	C(11) - C(12)	1.390(3)
C(11) - H(11)	0.948(17)	C(12) - H(12)	0.930(16)
C(13) - C(14)	1.403(3)	C(13) - C(18)	1.387(3)
C(14) - C(15)	1.388(3)	C(14) - O(2)	1.365(3)
C(15) - C(16)	1.372(4)	C(15) - H(15)	0.92(3)
C(16) - C(17)	1.359(4)	C(16) - H(16)	0.95(3)
C(17) - C(18)	1.402(3)	C(17) - H(17)	0.97(3)
C(18) - H(18)	0.96(2)	C(19) - C(20)	1.404(2)
C(19) - C(24)	1.384(2)	C(20) - C(21)	1.386(2)
C(20) - O(3)	1.365(2)	C(21) - C(22)	1.380(3)
C(21) - H(21)	0.933(17)	C(22) - C(23)	1.368(3)
C(22) - H(22)	0.968(19)	C(23) - C(24)	1.388(2)
C(23) - H(23)	0.973(16)	C(24) - H(24)	0.947(17)
C(25) - O(1)	1.425(2)	C(25) - H(25A)	0.97(3)
C(25) - H(25B)	0.97(2)	C(25) - H(25C)	0.94(3)
C(26) - O(2)	1.424(3)	C(26) - H(26A)	0.96(3)
C(26) - H(26B)	0.95(3)	C(26) - H(26C)	1.00(3)
C(27) - O(3)	1.427(3)	C(27) - H(27A)	0.930(19)
C(27) - H(27B)	1.02(3)	C(27) - H(27C)	0.98(3)

Table 22

Bond angles for 1,3,5-tri-(2-methoxyphenyl)-1,3,5-triazacyclohexane (43)

C(2)-N(1)-C(6)	112.4(2)	C(2)-N(1)-C(7)	118.4
C(6)-N(1)-C(7)	118.7(1)	C(2)-N(3)-C(4)	108.4(2)
C(2)-N(3)-C(13)	114.2(2)	C(4)-N(3)-C(13)	114.7(2)
C(4)-N(5)-C(6)	110.6(1)	C(4)-N(5)-C(19)	116.8(2)
C(6)-N(5)-C(19)	118.4(1)	N(1)-C(2)-N(3)	112.6(2)
N(1)-C(2)-H(2A)	106.8	N(1)-C(2)-H(2B)	110.2
N(3)-C(2)-H(2A)	107.6	N(3)-C(2)-H(2B)	110.0
H(2A)-C(2)-H(2B)	109.6	N(3)-C(4)-N(5)	112.3(2)
N(3)-C(4)-H(4A)	108.6	N(3)-C(4)-H(4B)	113.3
N(5)-C(4)-H(4A)	112.0	N(5)-C(4)-H(4B)	105.0
H(4A)-C(4)-H(4B)	105.5	N(1)-C(6)-N(5)	113.5(2)
N(1)-C(6)-H(6A)	109.0	N(1)-C(6)-H(6B)	107.9
N(5)-C(6)-H(6A)	109.4	N(5)-C(6)-H(6B)	107.3
H(6A)-C(6)-H(6B)	109.7	N(1)-C(7)-C(8)	117.8(2)
N(1)-C(7)-C(12)	123.3(2)	C(8)-C(7)-C(12)	118.7(2)
C(7)-C(8)-C(9)	119.9(2)	C(7)-C(8)-O(1)	115.8(2)
C(9)-C(8)-O(1)	124.3(2)	C(8)-C(9)-C(10)	120.1(2)
C(8)-C(9)-H(9)	120.0	C(10)-C(9)-H(9)	119.8
C(9)-C(10)-C(11)	120.5(2)	C(9)-C(10)-H(10)	120.1
C(11)-C(10)-H(10)	119.4	C(10)-C(11)-C(12)	119.9(2)
C(10)-C(11)-H(11)	122.1	C(12)-C(11)-H(11)	118.0
C(7)-C(12)-C(11)	120.9(2)	C(7)-C(12)-H(12)	117.3
C(11)-C(12)-H(12)	121.8	N(3)-C(13)-C(14)	118.6(2)
N(3)-C(13)-C(18)	123.2(2)	C(14)-C(13)-C(18)	118.1(2)
C(13)-C(14)-C(15)	120.2(2)	C(13)-C(14)-O(2)	115.4(2)
C(15)-C(14)-O(2)	124.3(2)	C(14)-C(15)-C(16)	120.4(3)
C(14)-C(15)-H(15)	115.5	C(16)-C(15)-H(15)	124.0
C(15)-C(16)-C(17)	120.6(2)	C(15)-C(16)-H(16)	122.0
C(17)-C(16)-H(16)	117.4	C(16)-C(17)-C(18)	119.9(2)
C(16)-C(17)-H(17)	120.1	C(18)-C(17)-H(17)	120.0
C(13)-C(18)-C(17)	120.8(2)	C(13)-C(18)-H(18)	119.9
C(17)-C(18)-H(18)	119.1	N(5)-C(19)-C(20)	118.4(2)
N(5)-C(19)-C(24)	123.2(2)	C(20)-C(19)-C(24)	118.2(2)
C(19)-C(20)-C(21)	120.2(2)	C(19)-C(20)-O(3)	116.5(2)
C(21)-C(20)-O(3)	123.2(2)	C(20)-C(21)-C(22)	120.1(2)
C(20)-C(21)-H(21)	121.2	C(22)-C(21)-H(21)	118.6
C(21)-C(22)-C(23)	120.4(2)	C(21)-C(22)-H(22)	118.3
C(23)-C(22)-H(22)	121.3	C(22)-C(23)-C(24)	119.8(2)
C(22)-C(23)-H(23)	121.0	C(24)-C(23)-H(23)	119.2
C(19)-C(24)-C(23)	121.2(2)	C(19)-C(24)-H(24)	120.5
C(23)-C(24)-H(24)	118.2	O(1)-C(25)-H(25A)	105.3
O(1)-C(25)-H(25B)	111.9	O(1)-C(25)-H(25C)	110.9
H(25A)-C(25)-H(25B)	109.9	H(25A)-C(25)-H(25C)	108.9
H(25B)-C(25)-H(25C)	109.8	O(2)-C(26)-H(26A)	109.9
O(2)-C(26)-H(26B)	107.9	O(2)-C(26)-H(26C)	103.6
H(26A)-C(26)-H(26B)	107.2	H(26A)-C(26)-H(26C)	110.3

H(26B)-C(26)-H(26C)	117.7	O(3)-C(27)-H(27A)	105.2
O(3)-C(27)-H(27B)	108.7	O(3)-C(27)-H(27C)	110.2
H(27A)-C(27)-H(27B)	109.1	H(27A)-C(27)-H(27C)	112.5
H(27B)-C(27)-H(27C)	110.9	C(8)-O(1)-C(25)	117.4(2)
C(14)-O(2)-C(26)	119.3(2)	C(20)-O(3)-C(27)	116.8(2)

Table 23

Fractional coordinates for 1,3,5-tri-(4-methoxyphenyl)-1,3,5-triazacyclohexane (45)

	x	y	z
N(1)	0.37834(8)	0.14412(8)	0.18294(57)
C(2)	0.35725(11)	0.20975(11)	0.28969(31)
N(3)	0.37743(9)	0.29049(9)	0.22094(27)
C(4)	0.33129(12)	0.29913(12)	0.07002(30)
N(5)	0.35247(9)	0.23412(10)	-0.03926(27)
C(6)	0.33300(11)	0.15532(12)	0.03307(33)
C(7)	0.46494(10)	0.11632(9)	0.17650(28)
C(8)	0.53060(10)	0.15129(10)	0.26301(28)
C(9)	0.61279(11)	0.11674(11)	0.26896(28)
C(10)	0.63054(11)	0.04740(10)	0.18310(27)
C(11)	0.56629(12)	0.01400(10)	0.08891(29)
C(12)	0.48465(11)	0.04713(9)	0.08727(29)
C(13)	0.36895(10)	0.35614(11)	0.32827(29)
C(14)	0.31741(11)	0.42410(11)	0.29970(30)
C(15)	0.31560(12)	0.48872(11)	0.40392(34)
C(16)	0.36425(10)	0.48801(11)	0.54013(33)
C(17)	0.41455(11)	0.42071(12)	0.57181(29)
C(18)	0.41683(11)	0.35632(11)	0.46778(30)
C(19)	0.43304(11)	0.23880(10)	-0.11865(30)
C(20)	0.49467(12)	0.29799(10)	-0.08891(30)
C(21)	0.57075(12)	0.30122(11)	-0.17439(30)
C(22)	0.58791(13)	0.24402(11)	-0.28879(30)
C(23)	0.52757(14)	0.18338(11)	-0.31730(31)
C(24)	0.45133(12)	0.18177(10)	-0.23615(30)
O(25)	0.70746(9)	0.00669(9)	0.18324(27)
O(26)	0.35723(10)	0.55512(9)	0.63516(29)
O(27)	0.66127(12)	0.24058(10)	-0.38103(31)
C(28)	0.77506(14)	0.04029(19)	0.27524(43)
C(29)	0.4121(2)	0.5599(2)	0.7682(5)
C(30)	0.7259(2)	0.2984(3)	-0.3510(5)
H(2A)	0.3906(15)	0.1985(12)	0.3901(31)
H(2B)	0.2900(13)	0.2087(11)	0.3052(28)
H(4A)	0.3464(12)	0.3540(13)	0.0227(29)
H(4B)	0.2688(15)	0.2950(11)	0.0913(32)
H(6A)	0.2713(14)	0.1536(11)	0.0568(31)
H(6B)	0.3463(13)	0.1093(13)	-0.0452(31)
H(8)	0.5205(15)	0.2008(13)	0.3119(30)
H(9)	0.6542(13)	0.1427(12)	0.3316(30)
H(11)	0.5816(12)	-0.0342(12)	0.0320(29)
H(12)	0.4379(12)	0.0217(11)	0.0233(30)
H(14)	0.2846(13)	0.4257(12)	0.2060(33)
H(15)	0.2781(13)	0.5368(11)	0.3838(31)
H(17)	0.4506(18)	0.4201(16)	0.6650(43)
H(18)	0.4525(15)	0.3077(18)	0.4941(32)
H(20)	0.4861(13)	0.3360(13)	-0.0125(31)

H(21)	0.6123(15)	0.3406(13)	-0.1486(32)
H(23)	0.5449(14)	0.13745(14)	-0.3965(36)
H(24)	0.4099(14)	0.1373(14)	-0.2572(33)
H(28A)	0.823(2)	0.002(2)	0.271(4)
H(28B)	0.754(2)	0.044(1)	0.386(6)
H(28C)	0.7864(17)	0.0911(17)	0.2435(45)
H(29A)	0.392(2)	0.511(2)	0.843(6)
H(29B)	0.470(2)	0.553(1)	0.746(4)
H(29C)	0.4092(19)	0.6131(19)	0.8248(45)
H(30A)	0.773(3)	0.283(2)	-0.420(6)
H(30B)	0.748(2)	0.290(2)	-0.250(5)
H(30C)	0.705(2)	0.348(2)	-0.371(6)

Table 24

Bond lengths for 1,3,5-tri-(4-methoxyphenyl)-1,3,5-triazacyclohexane (45)

N(1) - C(2)	1.444(3)	N(1) - C(6)	1.462(5)
N(1) - C(7)	1.420(2)	N(3) - C(2)	1.482(3)
N(3) - C(4)	1.471(4)	N(3) - C(13)	1.416(3)
N(5) - C(4)	1.450(3)	N(5) - C(6)	1.463(3)
N(5) - C(19)	1.421(3)	C(2) - H(2A)	1.01(3)
C(2) - H(2B)	1.05(3)	C(4) - H(4A)	1.01(3)
C(4) - H(4B)	0.99(3)	C(6) - H(6A)	0.98(3)
C(6) - H(6B)	1.03(3)	C(7) - C(8)	1.380(3)
C(7) - C(12)	1.398(3)	C(8) - C(9)	1.397(3)
C(8) - H(8)	0.93(3)	C(9) - C(10)	1.379(3)
C(9) - H(9)	0.94(3)	C(10) - C(11)	1.389(3)
C(10) - O(25)	1.368(3)	C(11) - C(12)	1.379(3)
C(11) - H(11)	0.96(3)	C(12) - H(12)	1.00(3)
C(13) - C(14)	1.394(3)	C(13) - C(18)	1.395(4)
C(14) - C(15)	1.380(4)	C(14) - H(14)	0.94(3)
C(15) - C(16)	1.378(4)	C(15) - H(15)	1.00(2)
C(16) - C(17)	1.380(3)	C(16) - O(26)	1.369(3)
C(17) - C(18)	1.376(4)	C(17) - H(17)	0.97(4)
C(18) - H(18)	1.00(3)	C(19) - C(20)	1.387(3)
C(19) - C(24)	1.395(3)	C(20) - C(21)	1.386(3)
C(20) - H(20)	0.91(3)	C(21) - C(22)	1.375(4)
C(21) - H(21)	0.94(3)	C(22) - C(23)	1.388(3)
C(22) - O(27)	1.381(4)	C(23) - C(24)	1.368(4)
C(23) - H(23)	1.04(3)	C(24) - H(24)	0.99(3)
C(28) - O(25)	1.418(4)	C(28) - H(28A)	0.97(4)
C(28) - H(28B)	0.99(5)	C(28) - H(28C)	0.89(3)
C(29) - O(26)	1.413(5)	C(29) - H(29A)	1.07(5)
C(29) - H(29B)	0.92(4)	C(29) - H(29C)	1.00(4)
C(30) - O(27)	1.405(5)	C(30) - H(30A)	0.96(5)
C(30) - H(30B)	0.93(5)	C(30) - H(30C)	0.89(4)

Table 25

Bond angles for 1,3,5-tri-(4-methoxyphenyl)-1,3,5-triazacyclohexane (45)

C(2)-N(1)-C(6)	109.8(2)	C(2)-N(1)-C(7)	118.6(3)
C(6)-N(1)-C(7)	117.6(4)	C(2)-N(3)-C(4)	108.9(2)
C(2)-N(3)-C(13)	114.2(2)	C(4)-N(3)-C(13)	116.0(2)
C(4)-N(5)-C(6)	109.8(2)	C(4)-N(5)-C(19)	117.4(2)
C(6)-N(5)-C(19)	115.3(2)	N(1)-C(2)-N(3)	112.0(3)
N(1)-C(2)-H(2A)	105.9(13)	N(1)-C(2)-H(2B)	106.9(12)
N(3)-C(2)-H(2A)	112.6(12)	N(3)-C(2)-H(2B)	105.8(11)
H(2A)-C(2)-H(2B)	113.6(19)	N(3)-C(4)-N(5)	111.8(2)
N(3)-C(4)-H(4A)	108.4(13)	N(3)-C(4)-H(4B)	108.2(16)
N(5)-C(4)-H(4A)	110.5(14)	N(5)-C(4)-H(4B)	106.7(13)
H(4A)-C(4)-H(4B)	111.1(16)	N(1)-C(6)-N(5)	112.0(2)
N(1)-C(6)-H(6A)	106.8(16)	N(1)-C(6)-H(6B)	111.8(14)
N(5)-C(6)-H(6A)	108.3(12)	N(5)-C(6)-H(6B)	109.9(14)
H(6A)-C(6)-H(6B)	107.9(18)	N(1)-C(7)-C(8)	123.0(3)
N(1)-C(7)-C(12)	119.3(2)	C(8)-C(7)-C(12)	117.6(2)
C(7)-C(8)-C(9)	121.6(2)	C(7)-C(8)-H(8)	118.6(15)
C(9)-C(8)-H(8)	119.7(15)	C(8)-C(9)-C(10)	119.9(2)
C(8)-C(9)-H(9)	117.5(13)	C(10)-C(9)-H(9)	122.5(13)
C(9)-C(10)-C(11)	119.0(2)	C(9)-C(10)-O(25)	125.3(2)
C(11)-C(10)-O(25)	115.7(2)	C(10)-C(11)-C(12)	120.6(2)
C(10)-C(11)-H(11)	115.9(13)	C(12)-C(11)-H(11)	123.4(13)
C(7)-C(12)-C(11)	121.1(3)	C(7)-C(12)-H(12)	118.4(12)
C(11)-C(12)-H(12)	120.5(12)	N(3)-C(13)-C(14)	123.5(2)
N(3)-C(13)-C(18)	119.7(2)	C(14)-C(13)-C(18)	116.8(2)
C(13)-C(14)-C(15)	121.1(30)	C(13)-C(14)-H(14)	118.5(13)
C(15)-C(14)-H(14)	120.4(13)	C(14)-C(15)-C(16)	121.1(2)
C(14)-C(15)-H(15)	120.9(15)	C(16)-C(15)-H(15)	118.0(15)
C(15)-C(16)-C(17)	118.6(3)	C(15)-C(16)-O(26)	116.2(2)
C(17)-C(16)-O(26)	125.2(3)	C(16)-C(17)-C(18)	120.4(3)
C(16)-C(17)-H(17)	119.6(17)	C(18)-C(17)-H(17)	119.9(17)
C(13)-C(18)-C(17)	121.9(2)	C(13)-C(18)-H(18)	118.9(16)
C(17)-C(18)-H(18)	119.1(16)	N(5)-C(19)-C(20)	124.0(2)
N(5)-C(19)-C(24)	118.6(2)	C(20)-C(19)-C(24)	117.4(2)
C(19)-C(20)-C(21)	121.3(2)	C(19)-C(20)-H(20)	120.7(14)
C(21)-C(20)-H(20)	118.0(14)	C(20)-C(21)-C(22)	120.4(2)
C(20)-C(21)-H(21)	119.3(16	C(22)-C(21)-H(21)	120.1(16)
C(21)-C(22)-C(23)	118.8(2)	C(21)-C(22)-O(27)	125.8(2)
C(23)-C(22)-O(27)	115.4(2)	C(22)-C(23)-C(24)	120.7(3)
C(22)-C(23)-H(23)	117.1(13)	C(24)-C(23)-H(23)	122.1(13)
C(19)-C(24)-C(23)	121.4(2)	C(19)-C(24)-H(24)	119.5(15)
C(23)-C(24)-H(24)	119.1(15)	O(25)-C(28)-H(28A)	107.3(20)
O(25)-C(28)-H(28B)	107.0(22)	O(25)-C(28)-H(28C)	110.1(21)
H(28A)-C(28)-H(28B)	109.4(30)	H(28A)-C(28)-H(28C)	115.8(26)
H(28B)-C(28)-H(28C)	106.9(27)	O(26)-C(29)-H(29A)	104.4(23)
O(26)-C(29)-H(29B)	114.4(23)	O(26)-C(29)-H(29C)	113.8(20)
H(29A)-C(29)-H(29B)	108.0(26)	H(29A)-C(29)-H(29C)	111.4(32)

H(29B)-C(29)-H(29C)	104.8(24)	O(27)-C(30)-H(30A)	104.6(26)
O(27)-C(30)-H(30B)	109.4(21)	O(27)-C(30)-H(30C)	108.5(24)
H(30A)-C(30)-H(30B)	103.6(38)	H(30A)-C(30)-H(30C)	113.7(40)
H(30B)-C(30)-H(30C)	116.3(39)	C(10)-O(25)-C(28)	117.1(2)
C(16)-O(26)-C(29)	117.7(3)	C(22)-O(27)-C(30)	117.3(3)

Appendix B

N.M.R. Spectra

Fig 14

^{1}H N.M.R. spectrum of 1,3,5-tri-(4-nitrophenyl) -1,3,5-triazacyclohexane (20)

^{1}H N.M.R. spectrum of N,N-bis-(4-nitrophenyl) diaminomethane (21)

Fig 15

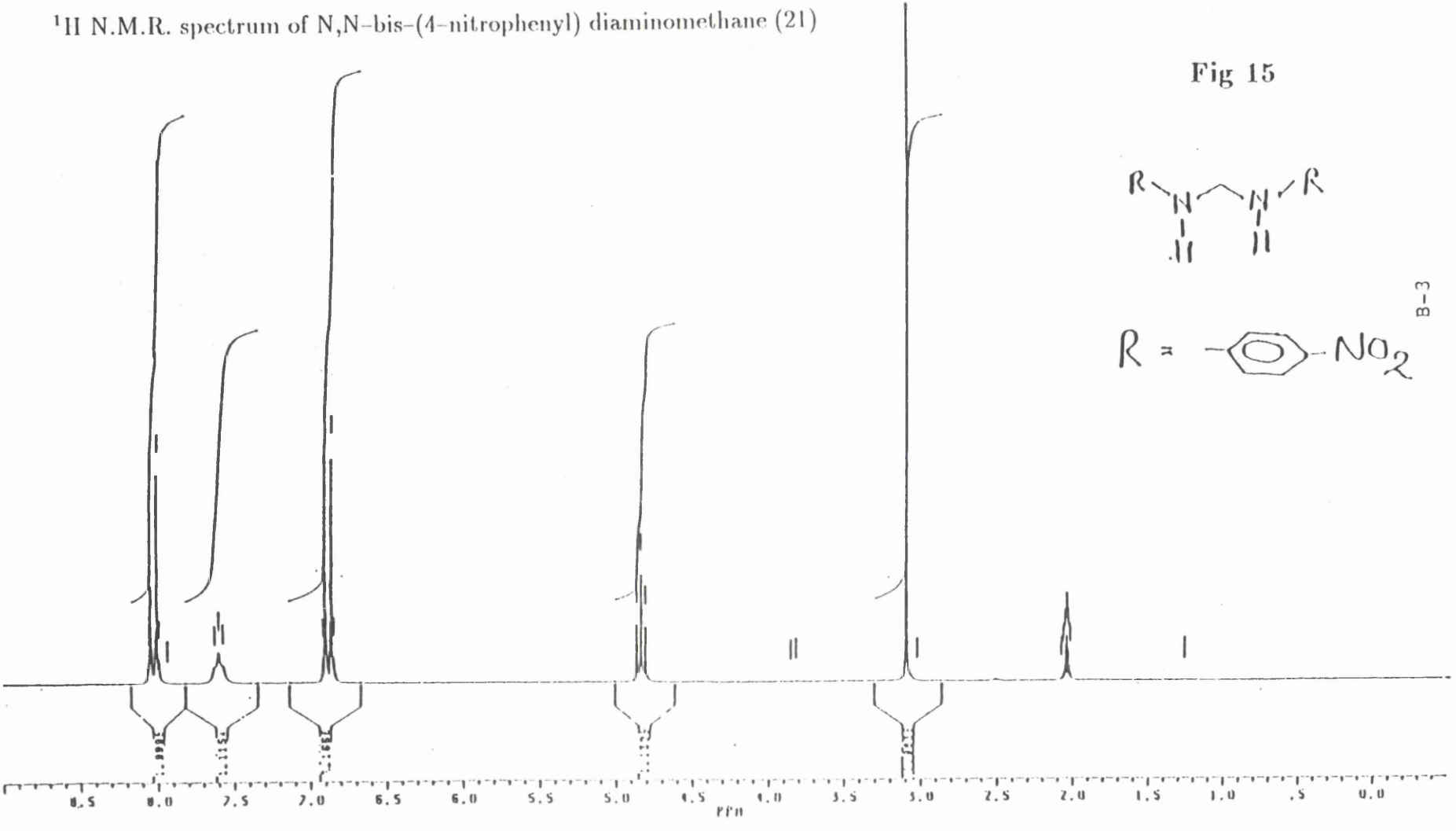
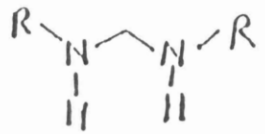
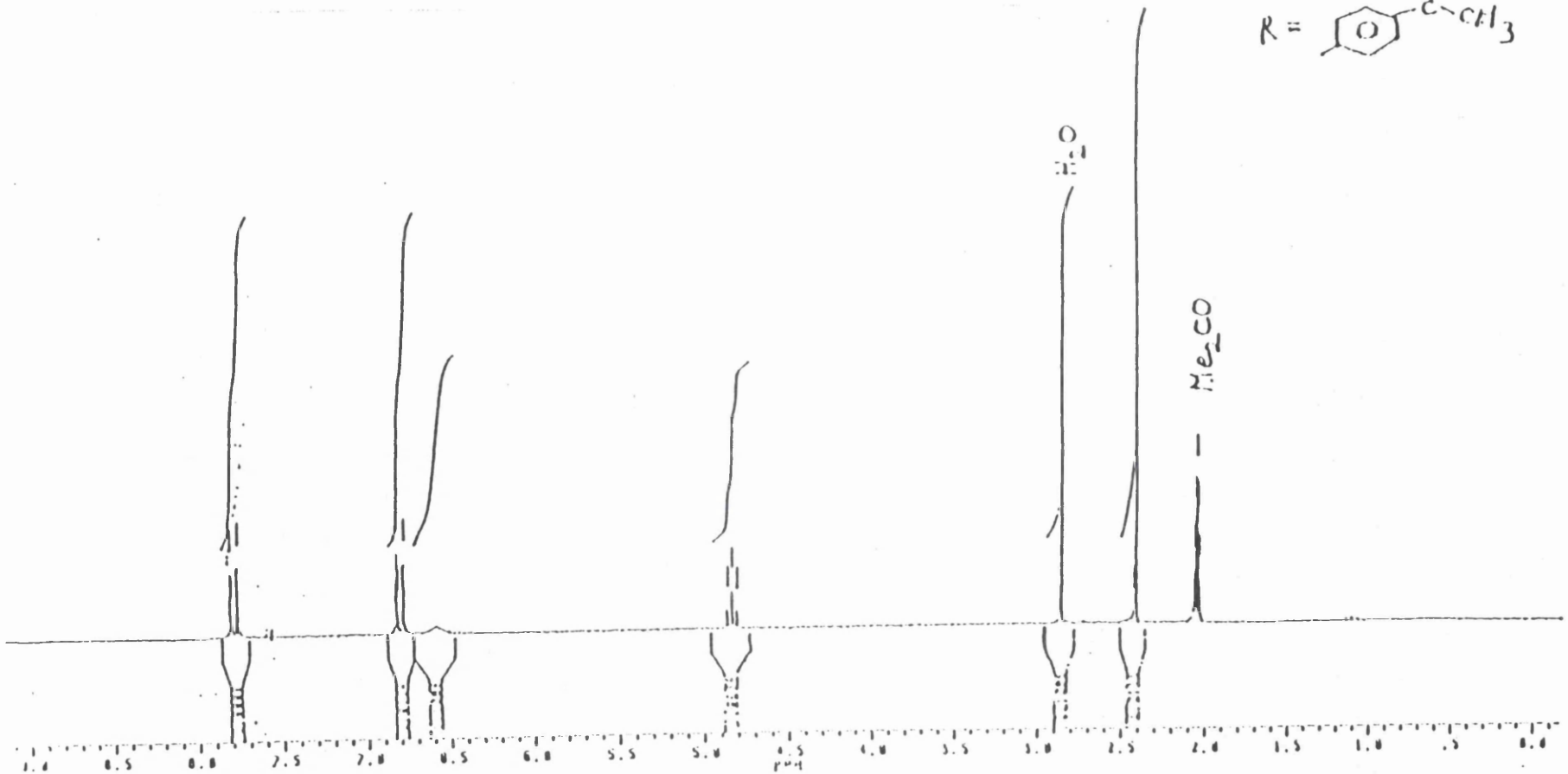


Fig 16

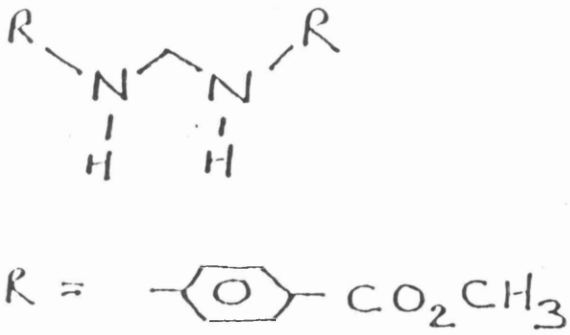


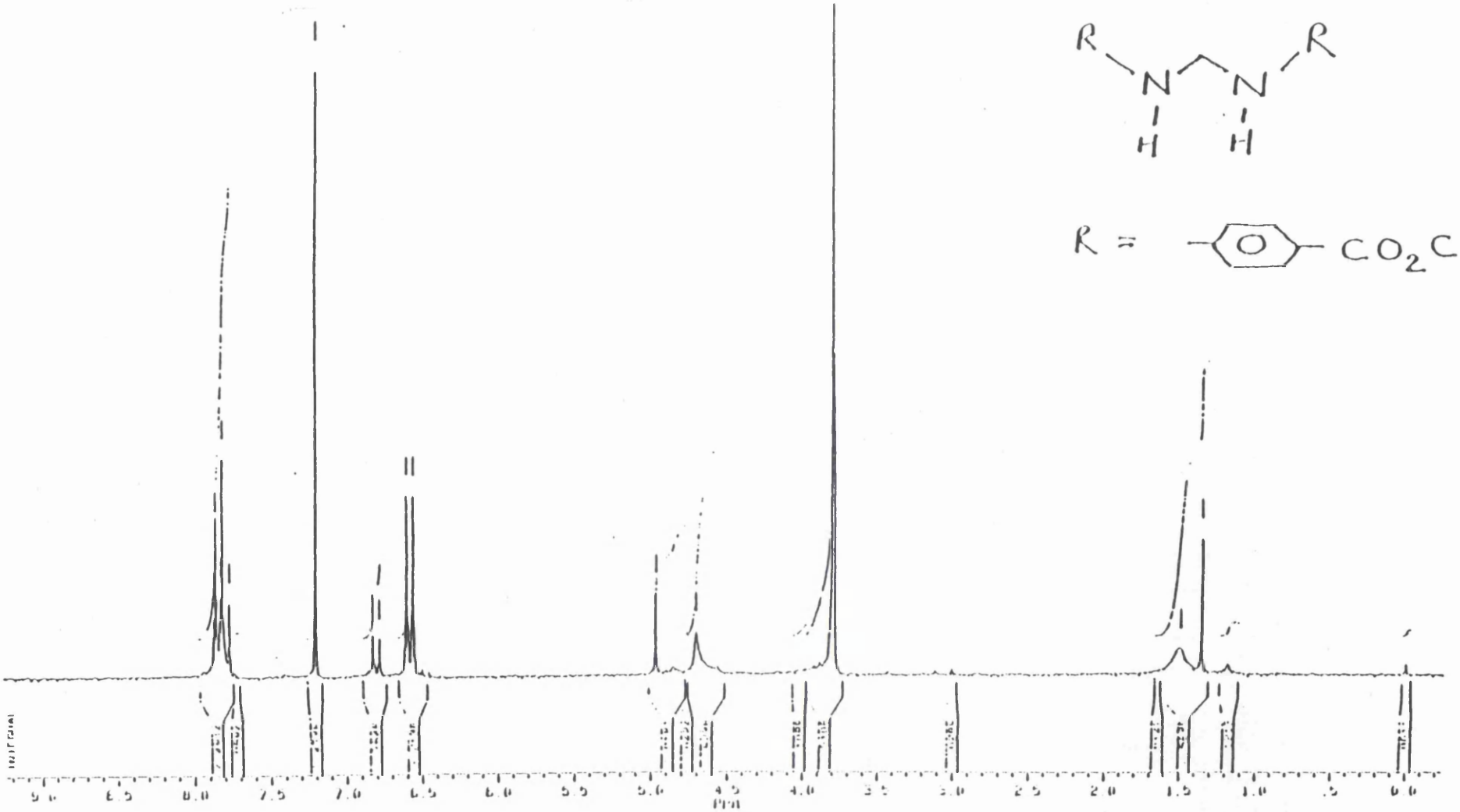
^{1}H N.M.R. spectrum of N,N–bis–(4–acetylphenyl) diaminomethane (32)



^{1}H N.M.R. spectrum of N,N–bis–(4–methoxycarbonylphenyl) diaminomethane (34)

Fig 17





^{1}H N.M.R. spectrum of 1,3,5–tri–(3–trifluoromethylphenyl)–1,3,5– triazacyclohexane (40)

Fig 18

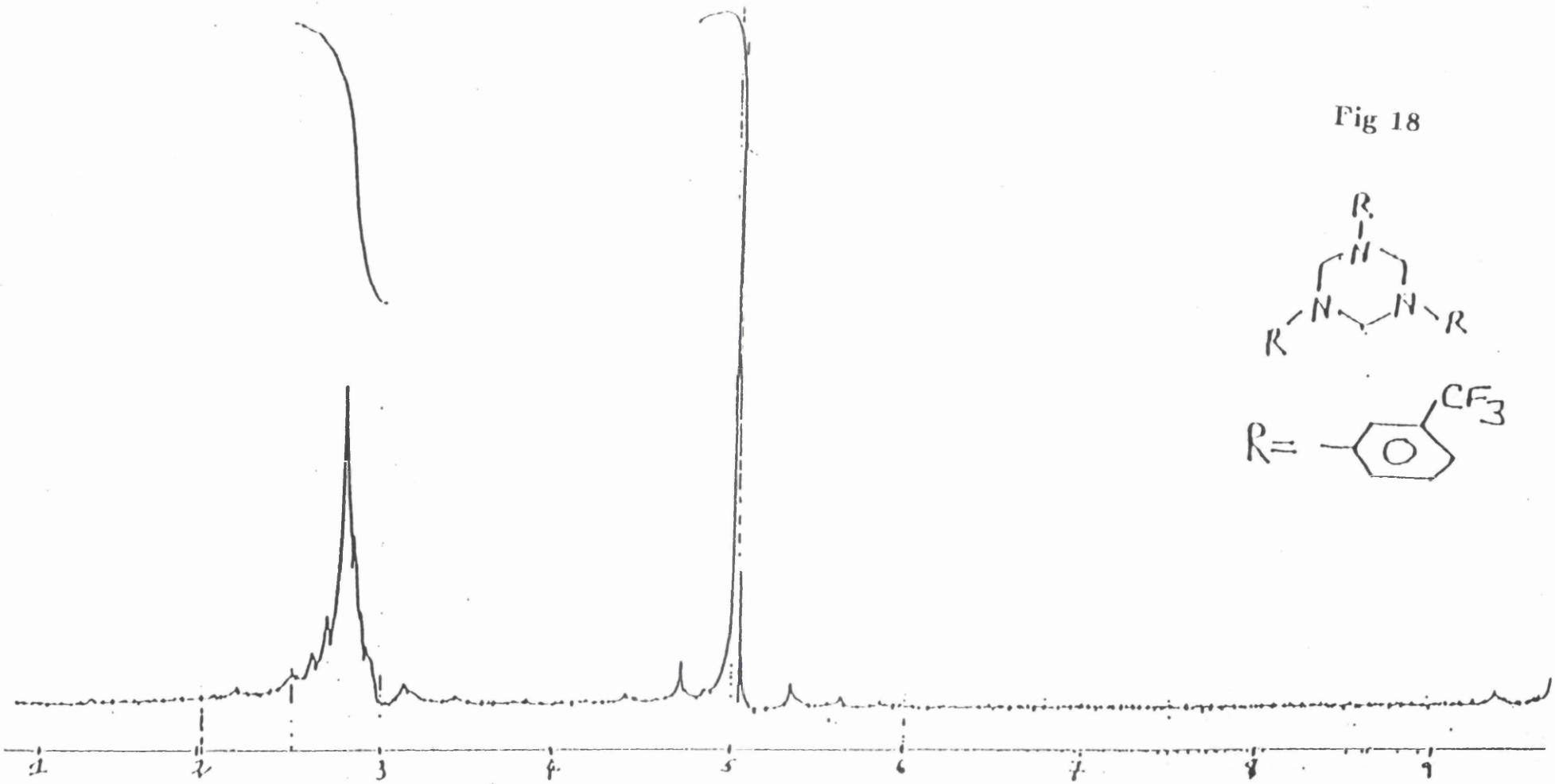
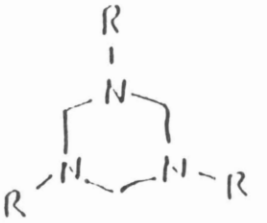


Fig 19



$R = -\langle O \rangle - CN$

^1H N.M.R. spectrum of 1,3,5–tri–(4–cyanophenyl)–1,3,5–triazacyclohexane (41)

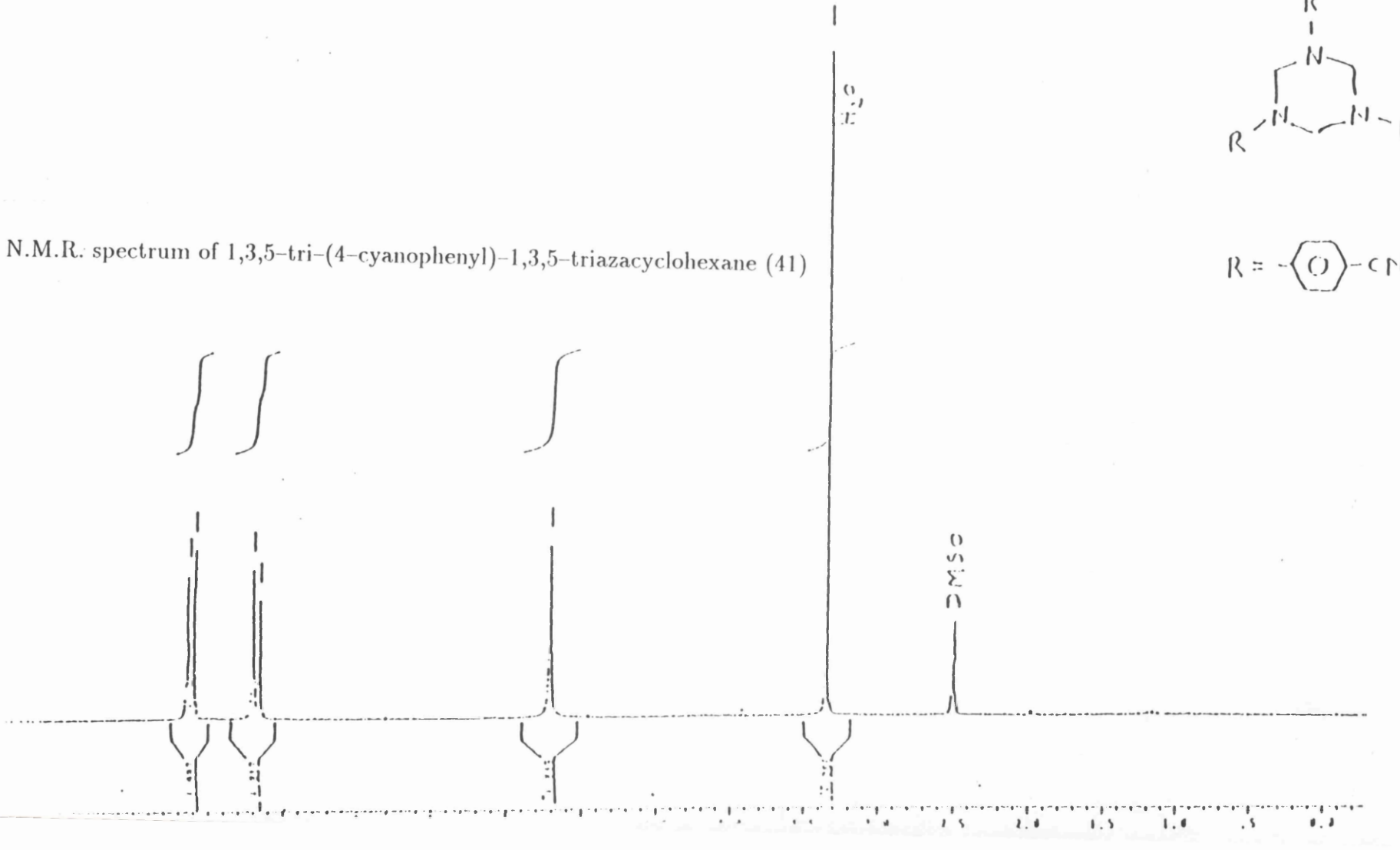
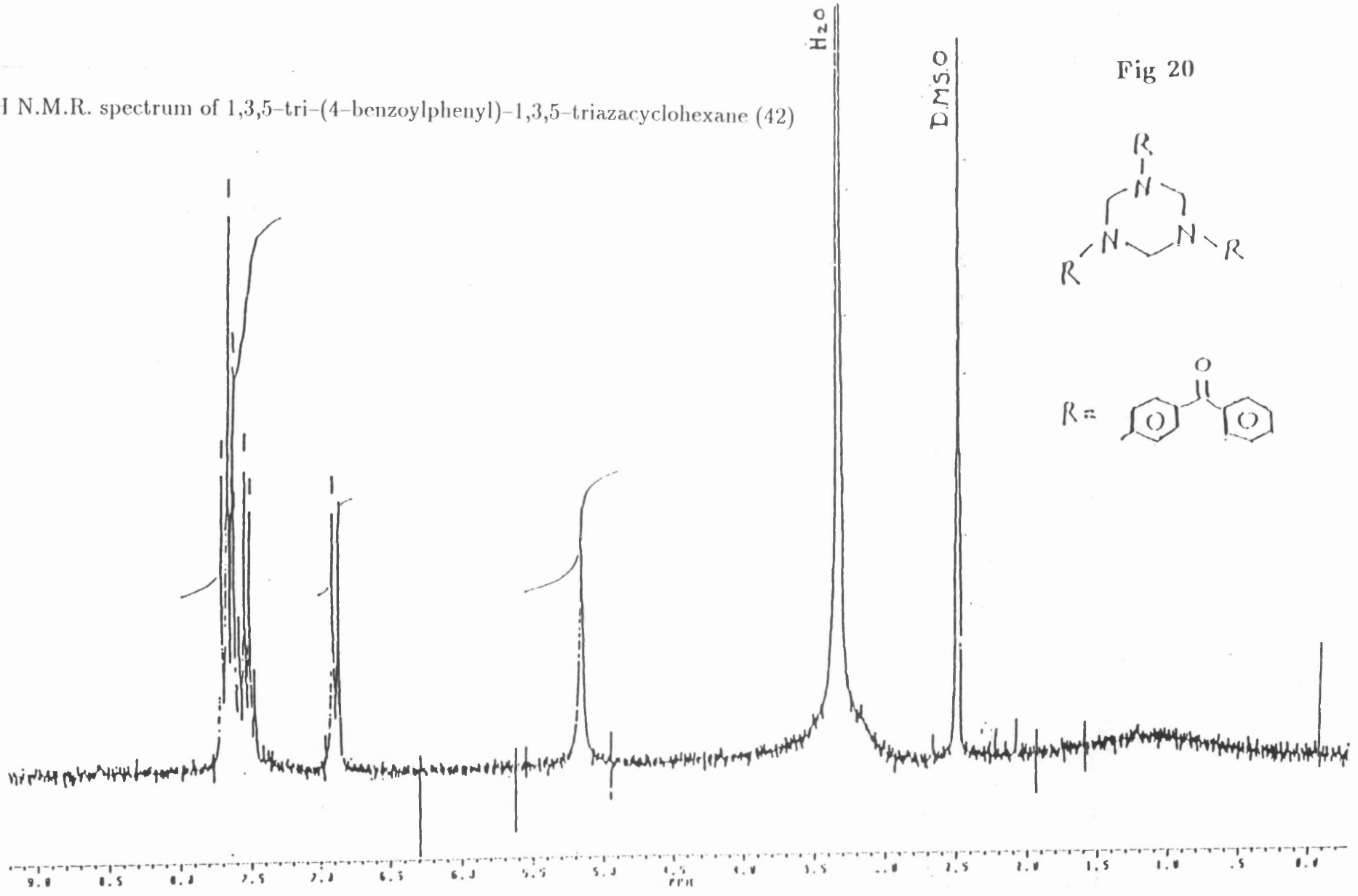


Fig 20

^{1}H N.M.R. spectrum of 1,3,5-tri-(4-benzoylphenyl)-1,3,5-triazacyclohexane (42)



. ^{1}H N.M.R. spectrum of 1,3,5-tri-(2-methoxyphenyl)-1,3,5-triazacyclohexane (43)

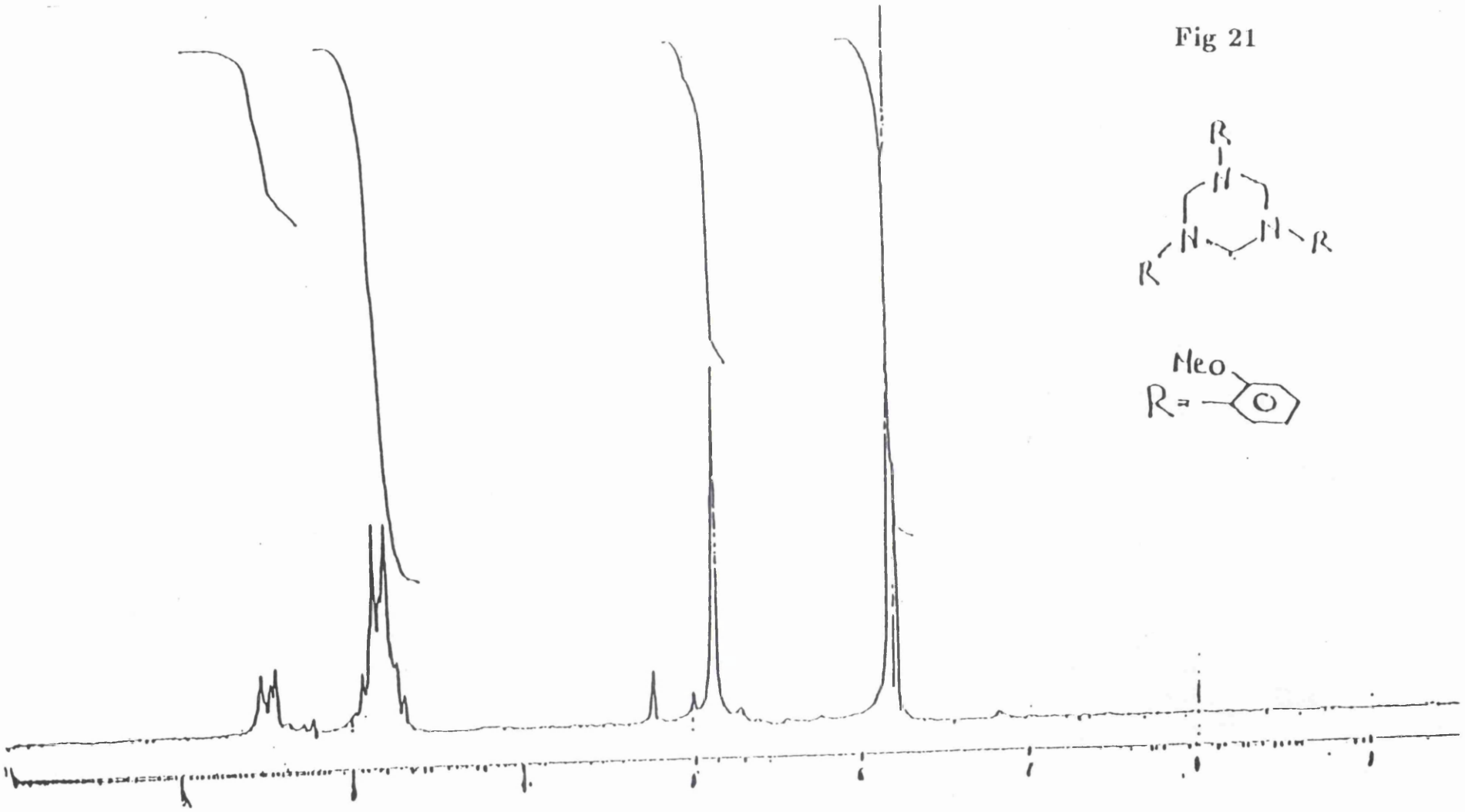


Fig 21

^{1}H N.M.R. spectrum of 1,3,5-tri-(4-methoxyphenyl)-1,3,5-triazacyclohexane (45) **Fig 22**